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For: OXYNITRIDE PHOSPHOR AND PRODUCTION PROCESS THEREOF, AND LIGHT-EMITTING DEVICE USING OXYNITRIDE PHOSPHOR		

VERIFICATION OF ENGLISH TRANSLATION

Commissioner for Patents
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Sir:

I, Keiichi GONJOU, declare that I am conversant in both the Japanese and English languages and that the English translation as attached hereto is an accurate translation of Japanese Patent Application No. 2002-381025 filed December 27, 2002.

Signed this 23rd day of May, 2008



Keiichi GONJOU

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Yes

[DOCUMENT] Specification

[TITLE OF THE INVENTION]

OXYNITRIDE PHOSPHOR AND PRODUCTION PROCESS THEREOF, AND
LIGHT-EMITTING DEVICE USING OXYNITRIDE PHOSPHOR

[CLAIMS]

[CLAIM 1]

An oxynitride phosphor comprising:

one or more of rare earth elements in which Eu is essential as an activator,

one or more of Group II elements selected from the group consisting of Ca, Sr, Ba
and Zn in which Ba is essential, and

one or more of Group IV elements selected from the group consisting of C, Si, Ge,
Sn, Ti, Zr and Hf in which Si is essential.

wherein said R is a molar ratio of the fore-mentioned Group II element : the
fore-mentioned R = 1 : 0.005 to 1 : 0.15 based on the fore-mentioned Group II element

[CLAIM 2]

The oxynitride phosphor according to claim 1, comprising O and N, wherein a
weight ratio is set so that N is within a range of 0.2 to 2.1 per 1 of O.

[CLAIM3]

The oxynitride phosphor according to claims 1 or 2; represented by a general
formula of $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$ (L in which Ba is essential are one or more Group II
elements selected from the group consisting of Ca, Sr, Ba and Zn and said M in which Si is
essential are one or more Group IV elements selected from the group consisting of C, Si, Ge,
Sn, Ti, Zr and Hf, O is an oxygen element. N is a nitrogen element. R is a rare earth
element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, and $1.5 < Z < 2.5$).

[CLAIM4]

The oxynitride phosphor represented by a general formula of
 $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)} \cdot R$ (L in which Ba is essential are one or more Group II
elements selected from the group consisting of Ca, Sr, Ba and Zn and said M in which Si is

essential are one or more Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf, Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, $0 < T < 0.5$, and $1.5 < Z < 2.5$).

[CLAIM5]

The oxynitride phosphor according to claims 3 or 4,
wherein said X, said Y and said Z are $X = 1$, $Y = 2$, and $Z = 2$.

[CLAIM6]

The oxynitride phosphor as in one of claims 1, 3 and 4,
wherein 70 weight % or more of said R is Eu.

[CLAIM7]

The oxynitride phosphor as in one of claims 1 to 6, which is excited by light from the excitation light source having a luminescence peak wavelength at 360nm to 480nm, and emits has a luminescence peak wavelength at a longer wavelength side than said luminescence peak wavelength.

[CLAIM8]

The oxynitride phosphor as in one of claims 1 to 7, having a luminescence a peak wavelength in a range of from blue green to green region.

[CLAIM9]

The oxynitride phosphor as in one of claims 1 to 8, of which 50 weight % or more is crystal.

[CLAIM10]

The oxynitride phosphor as in one of claims 1 to 9, wherein the luminescence intensity excited by light of about 460nm is higher than luminescence intensity excited by light of about 350nm.

[CLAIM11]

A process for production of an oxynitride phosphor comprising;
a first step of mixing raw materials containing the nitride of L (L in which Ba is

essential is at least one or more of Group II elements selected from the group consisting of Ca, Sr, Ba and Zn, the nitride of M (M in which Si is essential is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf), the oxide of M, and the oxide of R (R in which Eu is essential are one or more rare earth elements), and

a second step of firing the mixture obtained in said first step,

wherein said R and said L are in a molar ratio within a range of said nitride of L :
said oxide of R = 1 : 0.005 to 1 : 0.15.

[CLAIM12]

The process for production of an oxynitride phosphor according to claim 11,
wherein a nitride of R is used in place of said oxide of R, or together with said
oxide of R.

[CLAIM13]

The process for production of an oxynitride phosphor according to claims 11 or 12,
wherein a compound of Q (Q is at least one or more of Group III elements selected
from the group consisting of B, Al, Ga and In) is further mixed in said first step.

[CLAIM14]

The process for production of an oxynitride phosphor as in one of claims 11 to 13,
wherein said nitride of L, said nitride of M and said oxide of M are adjusted in
molar ratios of $0.5 < \text{the nitride of L} < 1.5$, $0.25 < \text{the nitride of M} < 1.75$ and $2.25 < \text{the oxide of M} < 3.75$.

[CLAIM15]

The process for production of an oxynitride phosphor according to claims 11 or 14,
wherein at least a portion of the raw material of said nitride of L is substituted with at
least either of the oxide of R and a nitride of R.

[CLAIM16]

The oxynitride phosphor produced by the process as in one of claims 11 to 15.

[CLAIM17]

A light-emitting device comprising;

an excitation light source of which luminescence wavelength is in a range of a short wavelength region of visible light to ultraviolet, and a phosphor which converts at least a portion of light from said excitation light source,

wherein said phosphor contains an oxynitride phosphor in which Ba is essential, said oxynitride phosphor having the luminescence peak wavelength at a blue green to green region.

[CLAIM18]

The light-emitting device according to claim 17,

wherein said excitation light source is a light-emitting element.

[CLAIM19]

The light-emitting device according to claim 18,

wherein said light-emitting element has a nitride semiconductor containing In.

[CLAIM20]

The light-emitting device according to claim 17,

wherein the oxynitride phosphor as in one of claims 1-10 and 16 is used as an oxynitride phosphor.

[CLAIM21]

The light-emitting device according to claim 17,

wherein said phosphor includes a second phosphor together with said oxynitride phosphor, said second phosphor carrying out the wavelength conversion of at least a portion of light from said excitation light source and having a luminescence spectrum including one or more peak wavelengths in visible region.

[CLAIM22]

The light-emitting device according to claim 21,

wherein said second phosphor has a luminance spectrum including at least one or more luminescence peak wavelengths from a blue region to red region.

[CLAIM23]

The light-emitting device as in one of claims 17 to 22,
wherein a light mixed of at least two lights of a portion of the light from said
excitation light source, the light from said oxynitride phosphor and the light from said
second phosphor.

[CLAIM24]

The light-emitting device as in one of claims 17 to 23,
which has a luminescence color being set at an intermediate luminescence color
from the peak wavelength of said excitation light source to the peak wavelength of said
oxynitride phosphor or the peak wavelength of said second phosphor.

[CLAIM25]

The light-emitting device according to claim 24,
wherein the luminescence color is white color.

[CLAIM26]

The light-emitting device as in one of claims 17 to 25,
wherein the luminescence spectrum has at least one or more luminescence peak
wavelengths in the ranges consisting of a range of 360 to 485nm, a range of 485 to 548nm
and a range of 548 to 730nm.

[CLAIM27]

The light-emitting device as in one of claims 17 to 25;
wherein the luminescence spectrum has at least one or more luminescence peak
wavelengths in the ranges consisting of a range of 360 to 485nm and a range of 485 to
548nm.

[CLAIM28]

The light-emitting device as in one of claims 17 to 27,
wherein the average rendering index (Ra) is 80 or more.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD TO WHICH THE INVENTION PERTAINS]

The present invention relates to a phosphor which emit a light by being excited by light, electromagnetic waves such as X-rays, electron beam, and specifically, relates to a light-emitting device for usual illuminations such as a fluorescent lamp, illuminations mounted on a car, back lights for liquid crystal, displays and the like. Specifically, the present invention relates to a white color and multi-color light-emitting device using a semiconductor light-emitting element.

[PRIOR ART]

[0002]

A light-emitting device using light-emitting elements is a small size and superior in electric power efficiency, and emits fresh color. Further, said light-emitting elements have characteristics that there is no fear of a burnt-out light bulb because of a semiconductor element and they are superior in initial drive property and resistant in vibration and the repetition of on-off lighting. Since the light-emitting elements have such superior characteristics, a light-emitting device using semiconductor light-emitting elements such as an LED and a LD has been utilized as various light sources.

[0003]

There is developed a light-emitting device which emits a luminescence color different from the light of the light-emitting elements by partially or wholly converting the wavelength of the light of the light-emitting elements and mixing said wavelength-converted light with the light of light-emitting elements not subjected to wavelength conversion to release light.

[0004]

Among these light-emitting devices, a white color light-emitting device has been required in wide fields such as usual illuminations such as a phosphorescent lamp, illuminations mounted on a car, displays and back lights for liquid crystal. Further, there is required a light-emitting device having various color tastes such as a pastel color by combining a semiconductor light-emitting element and a phosphor.

[0005]

The luminescence color of a light-emitting device using a white color semiconductor light-emitting element is obtained by the theory of color mixture. Blue light released from a light-emitting element is irradiated in a phosphor layer, then repeats absorption and scattering several times in the layer, and then, is released to outside. On the other hand, the blue light absorbed in the phosphor works as an excitation light source and emits yellow fluorescent light. The mixture of the yellow light and the blue light is visualized as white to human eyes.

[0006]

For example, a blue color light-emitting element is used as the light-emitting element, and a phosphor is thinly coated on the surface of said blue color light-emitting element. Said light-emitting element is a blue color light-emitting device using an InGaN-base material. Further, the phosphor uses a YAG-base phosphor represented by the composition formula of $(Y,Gd)_3(Al,Ga)_5O_{12}:Ce$.

[0007]

Further, there has been recently reported a white color light-emitting device combining a phosphor which emits blue light and a YAG-base phosphor which emits yellow light using light-emitting elements of visible light at a short wavelength side region. In this case, the YAG-base phosphor which emits yellow light is hardly excited by light of visible light at the short wavelength side region and does not emit light. Accordingly, a blue color-base phosphor is excited by said light-emitting element to emit blue light. Then, the YAG-base phosphor is excited by said blue light to emit yellow light. Thus, white color light is emitted by the color mixture of the blue light of the blue color-base phosphor with the yellow light of the YAG-base phosphor.

[0008]

Various phosphors are developed as the phosphor used in said light-emitting device.

[0009]

For example, an oxide-base phosphor using a rare earth metal element for a

luminescence center has been widely known, and a portion of the phosphor is already practically used. However, a nitride phosphor and an oxynitride phosphor are seldom studied, and a study report is scarcely reported. For example, there is an oxynitride glass phosphor which is represented by Si-O-N, Mg-Si-O-N, Ca-Al-Si-O-N and the like (JP-A-2001-214162 : hereinafter, referred to as the patent literature 1). Further, there is an oxynitride glass phosphor represented by Ca-Al-Si-O-N in which Eu was activated (JP-A-2002-76434 : hereinafter, referred to as the patent literature 2).

[0010]

[Patent Document 1] JP-A-2001-214162

[Patent Document 2] JP-A-2002-76434

[0011]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, conventional phosphors have low luminescence brightness and are insufficient for being used for a light-emitting device. In a light-emitting device using light-emitting elements at a near ultraviolet region as an excitation light source, there is used double step excitation that a blue light-base phosphor is excited by said light-emitting elements and the YAG-base phosphor is excited by said excited light, therefore while light having high efficiency is hardly obtained. Accordingly, there is desired a phosphor emitting green light to yellow light whose wavelength was directly converted by light of visible light at a short wavelength side region.

[0012]

Further, a white color light-emitting device combining a phosphor and a light-emitting element of visible light at a short wavelength side region is not produced yet and the light-emitting device practically used is not commercially available. Accordingly, a phosphor which efficiently emits light at a short wavelength side region of visible light is desired.

[0013]

However, a white color light-emitting device equipped with the blue color

light-emitting element and the YAG-base phosphor emits white color light formed by the color mixture of blue light nearby 460nm and yellow green light nearby 565nm, but luminescence intensity nearby 500nm is insufficient.

[0014]

Further, the above-mentioned oxynitride phosphors and the like described in the patent literatures 1 and 2 have low luminescence brightness and are insufficient for being used for the light-emitting device. Further, since the oxynitride glass phosphor is a glass body, it is hardly processed in general.

[0015]

Accordingly, an object of the present invention is to provide a phosphor which is excited by an excitation light source at an ultraviolet to visible light region and which has a blue green to yellow luminescence color that is wavelength converted, and to provide a light-emitting device using thereof. Further, the purpose of the present invention is to provide a light-emitting device having high luminescence efficiency and being superior in reproducibility.

[0016]

[MEANS FOR SOLVING PROBLEM]

To solve the problem, the present invention relates to an oxynitride phosphor comprising: one or more of rare earth elements in which Eu is essential as an activator; one or more of Group II elements selected from the group consisting of Ca, Sr, Ba and Zn in which Ba is essential; and one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf in which Si is essential, wherein said R is a molar ratio of the fore-mentioned Group II element : the fore-mentioned R = 1 : 0.005 to 1 : 0.15 based on the fore-mentioned Group II element.

[0017]

The oxynitride phosphors are excited by the excitation light source in a range from near ultraviolet to a short wavelength side region of visible light and absorb a portion of light from the excitation light source. The oxynitride phosphors which absorb a portion of

light from the excitation light source carry out the wavelength conversion. Said light whose wavelength was converted has a luminescence peak wavelength at a blue green to yellow region. Namely, the fore-mentioned oxynitride phosphors absorb the portion of light from light-emitting elements and emit light having luminescence spectra having luminescence peak wavelengths at a blue green to yellow region. Further, said first to third oxynitride phosphors have high luminescence efficiency, extremely efficiently convert the wavelengths of light from light-emitting elements, and can emit light.

[0018]

The oxynitride phosphor relates to an oxynitride phosphor comprising O and N, wherein a weight ratio is set so that N is within a range of 0.2 to 2.1 per 1 of O. With this, the phosphor which has a luminescence color in a range from green to yellow region by excited a light from the excitation light source can be provided.

[0019]

The oxynitride phosphor is represented by a general formula of $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$ (L in which Ba is essential are one or more Group II elements selected from the group consisting of Ca, Sr, Ba and Zn and said M in which Si is essential are one or more Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf, O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, and $1.5 < Z < 2.5$). The oxynitride phosphors are excited by light in a range from ultraviolet to a short wavelength side region of visible light and emit light at a green to yellow region. The oxynitride phosphor has a stability same as or more than YAG phosphor. Further, since the luminescent portion of the oxynitride phosphor is not a glass body (amorphous) but powder or particles having a crystal, its production and processing are easy. A phosphor having good luminescence efficiency can be provided by setting the fore-mentioned X, Y and Z within the above-mentioned range. That is, a crystal phase being the luminescent portion can be comparatively easily formed by setting the fore-mentioned X, Y and Z within the above-mentioned range. Contrast with this, the X, Y and Z without the above-mentioned range lowers the luminescence efficiency.

[0020]

The oxynitride phosphor may be represented by the general formula, $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z-a)}R$ or $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z-a)}R$ ($0 < a < 1$). Because the oxynitride phosphor may be short of Nitride. The crystallinity and the luminescent brightness is improved with a closing to 0.

[0021]

It is preferable that said X, said Y and said Z are $X = 1$, $Y = 2$, and $Z = 2$. This composition makes it possible to improve the crystallinity and the luminescent efficiency.

[0022]

Eu is preferably 70% by weight or more among R. The R which is a rare earth element is preferably Eu in order to obtain high luminescence efficiency. Eu of that range makes it possible to obtain high luminescence efficiency.

[0023]

The oxynitride phosphor relates to an oxynitride phosphor which is excited by light from the excitation light source having a luminescence peak wavelength at 360nm to 480nm, and emits has a luminescence peak wavelength at a longer wavelength side than said luminescence peak wavelength. The excitation light source of said rang makes it possible to provide a phosphor having high luminescence efficiency. The excitation light source having luminescence peak wavelengths at 240 to 480nm can be used. But the excitation light source having a luminescence peak wavelength at 360 to 470nm is preferably used. In particular, it is preferable to use the excitation light source having a luminescence peak wavelength at 380 to 420nm or 450 to 470nm which is used in a semiconductor light-emitting element.

[0024]

The oxynitride phosphors has a luminescence spectra at a blue green to green region. Further, even if the YAG-base phosphor having a luminescence peak wavelength at a yellow region is excited using excitation light having a wavelength nearby 400nm, it emits hardly light, but the oxynitride phosphors related to the present invention exhibit

high luminescence efficiency by the excitation light at said region. Additionally, when blue light is also used as the excitation light source, they exhibit high luminescence efficiency.

[0025]

The blue green to yellow red region is represented according to JIS Z8110. Specifically, the blue purple means a range of 380 to 455nm, the blue means a range of 455 to 485nm, the blue green means a range of 485 to 495nm, the green means a range of 495 to 548nm, the yellow green means a range of 548 to 573nm, the yellow means a range of 573 to 584nm, the yellow red means a range of 584 to 610nm, the red means a range of 610 to 780nm.

[0026]

The oxynitride phosphor related to an oxynitride phosphor which contains a crystal 50% by weight or more. The crystal is preferably contained by 50% by weight or more, and more preferably by 80% by weight or more. Namely, the crystalline phases are a principal luminescent portion, and when the portion of the crystalline phases being the luminescent portion is 50% by weight or more, luminescence with good efficiency is obtained. Thus, the more the crystalline phases are, the higher the luminescence brightness can be enhanced. Further, when the portion of the crystalline phases is much, its production and processing come to be easy.

[0027]

The oxynitride phosphors preferably have the excitation spectra in which luminescence intensity by light of 460nm is higher than luminescence intensity by light of 350nm. The phosphors excited by light at 460nm exhibit higher brightness than the phosphors excited by light at 350nm.

[0028]

The present invention relates to a process for production of an oxynitride phosphor comprising; a first step of mixing raw materials containing the nitride of L (L in which Ba is essential is at least one or more of Group II elements selected from the group

consisting of Ca, Sr, Ba and Zn, the nitride of M (M in which Si is essential is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf), the oxide of M, and the oxide of R (R in which Eu is essential are one or more rare earth elements), and a second step of firing the mixture obtained in said first step, wherein said R and said L are in a molar ratio within a range of said nitride of L : said oxide of R = 1 : 0.005 to 1 : 0.15. This makes it possible to provide phosphors easily produced and processed. Further, the phosphors with extremely good stability can be provided. Hereat, Li, Na, K, Rb, Cs, Mn, Re, Cu, Ag, Au and the like may be contained in the mother body of the oxynitride phosphors prepared by the production steps of the present production process or the present production process. Further, luminescence properties can be improved by enlarging the particle sizes of the appropriate amount of Li, Na, K and the like, enhancing the luminescence brightness, and the like, and once in a while, properties are occasionally improved. These Li, Na, K and the like may be contained in the raw material composition. Because the above-mentioned Li, Na, K and the like are scattered at the calcination step in the production steps of the oxynitride phosphors, and hardly contained in said composition. The above-mentioned Li, Na, K and the like are preferably 1000ppm or less based on the weight of the oxynitride phosphors. More preferably, it is preferably 100ppm or less. Further, other elements may be contained to a degree which does not damage the properties.

[0029]

The nitride of R is preferably used in place of the fore-mentioned oxide of R, or together with the fore-mentioned oxide of R. The oxynitride phosphors with the high luminescence brightness can be provided thereby.

[0030]

In the fore-mentioned first step, Q (Q is at least one of more of Group III elements selected from the group consisting of B, Al, Ga and In) is further preferably mixed. The particle diameter is enlarged thereby, and the improvement of the luminescence brightness can be designed.

[0031]

In the production process of the oxynitride phosphors related to the present invention, the fore-mentioned nitride of L, the fore-mentioned nitride of M and the fore-mentioned oxide of M are preferably adjusted at molar ratios of $0.5 < \text{the nitride of L} < 1.5$, $0.25 < \text{the nitride of M} < 1.75$ and $2.25 < \text{the oxide of M} < 3.75$. The oxynitride phosphors with the composition of $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$ or $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)} \cdot R$ can be provided thereby.

[0032]

At least the portion of the raw material comprising the fore-mentioned nitride of L is preferably substituted with at least either of the oxide of R and the nitride of R. The oxynitride phosphors with the high luminescence efficiency can be provided thereby.

[0033]

The present invention relates to an oxynitride phosphor produced by the production process of oxynitride phosphors as in one of claims 11 to 15.

[0034]

The present invention relates to a light-emitting device having an excitation light source which has a luminescence wavelength at a short wavelength region from ultraviolet to visible light and a phosphor which absorbs at least the portion of light from said excitation light source, converts the wavelength and has a luminescence color different from the luminescence color of the fore-mentioned excitation light source, wherein the oxynitride phosphors having the luminescence peak wavelength at a blue green to green region in which Ba is essential are contained in the fore-mentioned phosphor. According to this, the light-emitting device having high luminescence efficiency and excellent in color rendering can be provided. Further, the portion of light from the excitation light source having a luminescence wavelength at a short wavelength region from ultraviolet to visible light and the portion of light from the oxynitride phosphor having the luminescence peak wavelength at a blue green to green region become color mixture light to be able to provide the light-emitting device having a luminescence color at a blue purple to green region.

[0035]

The region from ultra-violet to a short wavelength side region of visible light is a range 240 to 480nm.

[0036]

The fore-mentioned excitation light source is preferably light-emitting elements. Namely, the light-emitting elements are small size, have good electric power efficiency, and emit bright color light. Further, said light-emitting elements have no fear of a burnt-out light bulb because of a semiconductor element. Further, they have characteristics that they are superior in initial drive property and resistant in vibration and the repetition of on-off lighting. Accordingly, it is preferable to combine the light-emitting elements with the oxynitride phosphors.

[0037]

The luminescent layer of the fore-mentioned light-emitting elements has preferably a nitride semiconductor containing In. The light-emitting elements release light having the luminescence peak wavelengths at 350 to 410nm, and the fore-mentioned oxynitride phosphors are efficiently excited by the light from said light-emitting elements to exhibit a fixed luminescence color. Since the luminescence with high intensity is obtained by being excited by light nearby 350 to 410nm, the light-emitting elements at said wavelength region are suitable. Further, since the light-emitting elements can make the width of the luminescence spectra narrow, the oxynitride phosphors can be efficiently excited, and light substantially having no color tone change can be released from the light-emitting device.

[0038]

The oxynitride phosphor as in one of claims 1 to 10 is preferably used as an oxynitride phosphor.

[0039]

The present invention relates to a light-emitting device in which the phosphor includes the second phosphor together with the fore-mentioned oxynitride phosphors.

The second phosphor carries out the wavelength conversion of at least the portion of light from the fore-mentioned excitation light sources and the fore-mentioned oxynitride phosphors. Thus, there can be provided the light-emitting device having a luminescence color at a visible light region by the color mixture of the light from the fore-mentioned excitation light sources, the fore-mentioned oxynitride phosphors and light from the second phosphor. The light-emitting device thus constituted can release a desired luminescence color so far as it is within a wavelength region from the luminescence color of the excitation light sources to the luminescence color of the oxynitride phosphors or the luminescence color of the second phosphor.

[0040]

The second phosphor may have at least one or more of the luminescence peak wavelengths from a blue region to green, yellow and red regions, thereby realizing a desired luminescence color. In particular, various luminescence colors can be realized by combining three primary colors of the green color of the oxynitride phosphors which were excited by the excitation light sources having the luminescence peak wavelengths in a range from ultraviolet to a short wavelength side region of visible light, with the blue color and red color of the second phosphor. Further, the light-emitting device may be a light-emitting device comprising the combination of 2 kinds of colors such as a green color with red color and a green color with yellow color.

[0041]

The fore-mentioned second phosphor is preferably at least one or more selected from an alkali earth halogen apatite phosphor, an alkali earth metal borate halogen phosphor, an alkali earth metal aluminate phosphor, an alkali earth silicate, an alkali earth sulfide, an alkali earth thiogallate, an alkali earth silicone nitride, and a germanic acid salt which are mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn; or a rare earth aluminate and a rare earth silicate which are mainly activated by the Lanthanide series element such as Ce; an organic and organic complex which are mainly activated by elements such as the

Lanthanide series element such as Eu. The light-emitting device having the high luminescence brightness and high luminescence efficiency such as quantum efficiency can be provided thereby. Further, the light-emitting device having good color rendering can be provided. Provided that the second phosphor is not limited by the above descriptions, and can use phosphors which emit light having various color tastes.

[0042]

The light-emitting device releases preferably light by mixing at least 2 or more of lights among the portion of the light from the fore-mentioned excitation light source, the light from the fore-mentioned oxynitride phosphor and the light from the fore-mentioned second phosphor. The luminescence color of the light-emitting device is adjusted thereby, and a desired luminescence color can be released. In particular, when the light-emitting elements which emit light at an ultraviolet region are used, the luminescence color at the ultraviolet region can be hardly viewed by human eyes. Accordingly, the luminescence color by mixing the light from the fore-mentioned oxynitride phosphor and the light from the fore-mentioned second phosphor is exhibited. Since said luminescence color is determined only by the phosphor, the adjustment of the luminescence color is extremely carried out easily. Wherein the phosphor is represented as the second phosphor, but the second phosphor is not limited to only one kind, and several kinds of phosphors may be contained. The finer chromaticity adjustment is possible by containing several kinds of phosphors. Further, in particular, when the light-emitting elements at a short wavelength region from ultraviolet to visible light are used, the lights from said light-emitting elements are little felt as a color taste for human eyes, therefore the deviation of chromaticity caused by production deviation can be lessened.

[0043]

The luminescence color of the light-emitting device can be set at an intermediate luminescence color from the peak wavelength which the fore-mentioned excitation light source has, to the peak wavelength which the fore-mentioned oxynitride phosphors have, or the peak wavelength which the fore-mentioned second phosphor has. The excitation

light source has the luminescence spectrum at a shorter wavelength side than the oxynitride phosphors or the second phosphor, and has high energy. The light-emitting device containing the fore-mentioned second phosphor can release the luminescence color from the high energy region to the low energy region of the oxynitride phosphors and the second phosphor. In particular, it exhibits the luminescence color from the luminescence peak wavelength of light-emitting elements to the first luminescence peak wavelength of the oxynitride phosphors, or the second luminescence peak wave which the second phosphor has. For example, when the luminescence peak wavelength of the light-emitting elements is situated at a blue region, the luminescence peak wavelength of the oxynitride phosphors excited is situated at a green region, and the luminescence peak wavelength of the second phosphor excited is situated at a red region, a white luminescence color can be exhibited by the color mixture of three colors. As a different example, when the luminescence peak wavelength of the light-emitting elements is situated at an ultraviolet region, the luminescence peak wavelength of the oxynitride phosphors excited is situated at a green region, and the luminescence peak wavelengths of the second phosphor excited are situated at yellow and red regions, a slightly yellowish white luminescence color and a multi-color base luminescence color can be realized. The luminescence color from a color taste nearby the luminescence color of the oxynitride phosphors, to a color taste nearby the luminescence color of the second phosphor can be realized by changing the compounding amount of the oxynitride phosphors and the second phosphor. Further, when the second phosphor has 2 or more of the luminescence peak wavelengths, there is realized the light-emitting device exhibiting a luminescence color between the luminescence peak wavelength which the light-emitting elements have, the luminescence peak wavelength which the oxynitride phosphors have, and 2 or more of the luminescence peak wavelengths which the second phosphor has. The second phosphor is not only used alone, but also 2 or more can be used in combination. Not only a light-emitting device emitting white light but also a light-emitting device emitting light with various color tastes such as a pastel color have been recently desired. According to

the light-emitting device of the present invention, there can be provided the light-emitting device having a desired color taste by variously combining the oxynitride phosphors which emit green light, the phosphor which emits red light, and the phosphor which emits blue light. In the light-emitting device related to the present invention, various color tastes can be realized not only by a process of changing the kind of phosphors, but also by a process of changing the compounding ratio of phosphors combined, a process of changing the coating process of phosphors on an excitation light source, a process of adjusting the lighting time of an excitation light source, and the like.

[0044]

The fore-mentioned intermediate luminescence color is preferable a white color, more preferably a white color nearby the locus of black body radiation in particular. The white color base light-emitting device can be used for various uses such as illuminations, the back light of liquid crystal and displays.

[0045]

Further, the light-emitting device is preferably a light-emitting device having a luminescence spectrum having at least one or more of the luminescence peak wavelengths at 360 to 485nm, 485 to 548nm and 548 to 730nm. There can be provided the light-emitting device which emits light with a desired color taste by combining a blue color, a green color, a red color and the like which are three primary colors. Further, the color rendering can be improved by combining several phosphors. Because in case of the same white color luminescence, there exist also a yellowish white color and a bluish white color.

[0046]

The light-emitting device is preferably a light-emitting device having a luminescence spectrum having at least one or more of the luminescence peak wavelengths at 360 to 485nm and 485 to 548nm. For example, there can be obtained the light-emitting device which emits white light by combining a blue light-emitting element and a YAG-base phosphor, but light nearby 500nm is insufficient. Accordingly, there can be provided the light-emitting device having excellent color rendering by containing the oxynitride

phosphor which emits light nearby 500nm.

[0047]

The light-emitting device is preferably the average rendering index (Ra) of 80 or more. The light-emitting device having excellent color rendering can be provided thereby. In particular, the light-emitting device whose specific color rendering (R9) was improved can be provided.

[0048]

As described above, the oxynitride phosphors related to the present invention can provide a phosphor which is excited by light in a range from near ultraviolet to a short wavelength side region of visible light and emit light at a blue green to yellow region can provided and the light-emitting device with extremely good luminescence efficiency can be provided. It is possible to provide oxynitride phosphors which has a crystal produced and processed with ease. The oxynitride excellent in stability and reproductively can be provided. In addition, a new production process of the oxynitride phosphor can be provided. Moreover, the present invention has a technical meaning that the light emitting device having a desired luminescent color can be provided by combining an oxynitride phosphor and a second phosphor.

[0049]

[MODE FOR CARRING OUT THE INVENTION]

The light-emitting device related to the present invention and the oxynitride phosphor used for said light-emitting device, and the production process are illustrated below using the modes of operation and Examples. Provided that the present invention is not limited to embodiments and examples.

[0050]

The light-emitting device related to the present invention is a light-emitting device has at least a light-emitting element and the first phosphor converting the wavelength of at least the portion of light from said light-emitting element. The specific light emitting device will be described as an Example refer to Fig. 1. Fig. 1 is a section

view showing the constitution of the light-emitting device related to the present invention. The relation between the name of color and the chromaticity coordinate is according to JIS Z8110.

[0051]

(Excitation light source)

An excitation light source which has at least one or more of luminescence peak wavelengths in a range of a short wavelength side region of visible light to near-ultraviolet. The excitation light source which has the luminescence peak wavelengths in said range can be used without limitation. While a lamp and a semiconductor light emitting element are given as the excitation light source, it is preferable that the semiconductor light emitting element is used.

[0052]

(Light emitting element)

The light-emitting device of Embodiment 1 is composed of a semiconductor layer 2 laminated on a sapphire substrate 1, lead frames 13 electrically connected with electro-conductive wires 14 extending from positive and negative electrodes formed on the semiconductor layer 2, a phosphor 11 and a coating member 12 formed in a cup of the lead frame 13a so as to cover outer edge of the light emitting element 10 composed of the semiconductor layer 2 and the sapphire substrate 1 and a mold member 15 covering the phosphor 11 and outer surface of the lead frame 13.

[0053]

The semiconductor layer 2 is formed on the sapphire substrate 1 and the positive and negative electrodes 3 is formed on the same plane side of the semiconductor layer 2. A luminescent layer (not illustrated) is formed in the semiconductor layer 2. The luminescent layer has a spectrum of which luminescence peak wavelength is 500nm or less at an ultraviolet to blue region.

[0054]

The light-emitting element 10 is set in a die bonder, and face-up is carried out for

the lead frame 13a to be die-bonded (adhered). After the die-bonding, the lead frames 13 are transferred to a wire bonder, the negative electrode 3 of the light-emitting element is wire-bonded by a gold wire with the lead frame 13a which was provided in the cup, and the positive electrode 3 is wire-bonded with another lead frame 13b.

[0055]

Then, it is transferred to a mold equipment, and the phosphor 11 and the coating member 12 are injected in the cup of the lead frames 13 with the dispenser of the mold equipment. At this time, the phosphor 11 and the coating member 12 are preliminarily mixed at a fixed proportion homogeneously.

[0056]

After coating, the lead frames 13 are immersed in a mold frame where the mold member 15 was preliminarily injected, then the mold frame is removed and a resin is cured to prepare the cannonball type light-emitting device which is shown in Fig. 1.

[0057]

(Light emitting device)

A light emitting device of Embodiment 2 different from the light emitting device of Embodiment 1 is described in detail. The light emitting device according to the present invention is shown in Fig. 2. The light-emitting device of Embodiment 2 is a surface mounting type light-emitting device. In the light-emitting device of Embodiment 2, a nitride semiconductor light-emitting element which emits light at an ultraviolet region can be used as the light-emitting element 101, and a nitride semiconductor light-emitting element which emits light at a blue region can be also used. Hereat, the light-emitting element 101 which emits light at an ultraviolet region is illustrated as an example. In Embodiment 2, the light-emitting element 101 is a nitride semiconductor light-emitting element which has an InGaN semiconductor whose luminescence peak wavelength is about 370nm as a luminescent layer. The more specific LED element structure has a structure in which a luminescent layer having a single quantum well structure including an n-GaN layer being an undoped nitride semiconductor, a GaN layer in which an Si doped

n-electrode is formed to be an n-contact layer, an n-GaN layer being an undoped nitride semiconductor, an n-AlGaN layer being a nitride semiconductor and an InGaN well layer was laminated on a sapphire substrate. An AlGaN layer as an Mg doped p-clad layer and a GaN layer being an Mg doped p-contact layer are laminated in order on the luminescent layer. {Further, a buffer layer which was obtained by growing a GaN layer at low temperature is formed on a sapphire substrate. Further, the p-semiconductor is annealed at 400°C or more after coating.} In the above-mentioned laminated structure, the surfaces of the respective p-n-contact layers are exposed on the nitride semiconductor on the sapphire substrate by etching at the same face side. An n-electrode is formed in a belt shape on the n-contact layer exposed, and a transparent p-electrode comprising a metal thin film is formed on almost the whole surface of the residual p-contact layer. Further, a pedestal electrode is formed on the transparent p-electrode in parallel with the n-electrode using a sputtering process.

[0058]

There is used the package 105 made of kovar having a concave portion at a central part and comprising a base portion in which the lead electrode 102 made of kovar was inserted to be fixed in insulating hermetic seal at the both sides of the fore-mentioned concave portion. An Ni/Ag layer is provided on the surfaces of the fore-mentioned package 105 and the lead electrode 102. The above-mentioned light-emitting element 101 is die-bonded in the concave portion of the package 105 with an Ag-Sn alloy. All of the constitution members of the light-emitting device can be made by inorganic substances by composing thus, therefore even if the luminescence released from the light-emitting element 101 was at an ultraviolet region or a visible light short wavelength region, the light-emitting device having greatly high reliability is obtained.

[0059] Then, the respective electrodes of the light-emitting element 101 die-bonded are electrically connected with the respective lead electrodes 102 exposed from the bottom face of the package concave portion, with the Ag wire 104 respectively. After sufficiently removing moisture in the package concave portion, it is sealed with the lid 106 made of

kovar which has the glass window portion 107 at a central portion to carry out seam welding. The phosphor 108 containing $\text{CaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$, $(\text{Y}_{0.8}\text{Gd}_{0.2})_3\text{Al}_5\text{O}_{12}\cdot\text{Ce}$ and the like is preliminarily contained in a slurry consisting of 90% by weight of nitrocellulose and 10% by weight of γ -alumina, the mixture is coated on the back face of the transparent window portion 107 of the lid 106, and the color conversion member is constituted by curing by heating at 220°C for 30 minutes. When light is emitted from the light-emitting device thus formed, there can be prepared a light-emitting diode which can emit white light at high brightness. There can be prepared the light-emitting device which adjusts extremely easily chromaticity and is excellent in productivity and reliability, thereby. The respective constitutions of the present invention are specifically illustrated.

[0060]

The respective constitutions of the present invention are specifically illustrated.

[0061]

{Phosphor 11, 108}

The phosphor 11, 108 includes an oxynitride phosphor. The phosphor 11, 108 which includes a second phosphor in addition to the oxynitride phosphor may be used. The oxynitride phosphor related to the present invention uses a rare earth element as an activator. Namely, the oxynitride phosphor related to the present invention uses at least one or more of rare earth elements in which Eu is essential as an activator, and contains at least one or more of Group II elements selected from the group consisting of Ca, Sr, Ba and Zn in which Ba is essential, and at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf in which Si is essential. The combination of said elements is arbitrary but the phosphor having the composition below is preferable. The oxynitride phosphor is represented by the general formula of $\text{L}_x\text{M}_y\text{O}_z\text{N}_{((2/3)X+(4/3)Y-(2/3)Z)}\cdot\text{R}$, or $\text{L}_x\text{M}_y\text{Q}_t\text{O}_z\text{N}_{((2/3)X+(4/3)Y+T-(2/3)Z)}\cdot\text{R}$ (wherein L is at least one or more of Group II elements selected from the group consisting of Ca, Sr, Ba and Zn in which Ba is essential. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf in which Si is essential. Q is at least one or more of

Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is at least one or more of rare earth elements in which Eu is essential.). Further, the phosphor of Embodiment 6 exhibits high brightness within ranges of $0.5 < X < 1.5$, $1.5 < Y < 2.5$, $0 < T < 0.5$, and $1.5 < Z < 2.5$ in like manner as Embodiment 1. Further, among the general formula, the fore-mentioned X, the fore-mentioned Y and the fore-mentioned Z are preferably $0.8 < X < 1.2$, $1.8 < Y < 2.2$, $0 < T < 0.5$, and $1.7 < Z < 2.2$, and in particular, the oxynitride phosphor in which the fore-mentioned X, the fore-mentioned Y and the fore-mentioned Z are represented by $X = 1$, $Y = 2$, and $Z = 2$ is preferable because it exhibits high brightness. However, the present invention is not limited to the above-mentioned ranges. Specifically, as the oxynitride phosphor of Embodiment 6, there are mentioned $\text{BaSi}_{1.8}\text{Ge}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.9}\text{Ge}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.8}\text{Co}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.9}\text{Co}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.8}\text{Ti}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.9}\text{Ti}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.8}\text{Sn}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{BaSi}_{1.9}\text{Sn}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{Ba}_{0.9}\text{Zn}_{0.1}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Si}_{1.8}\text{Ge}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$, $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Si}_{1.8}\text{Ge}_{0.2}\text{O}_2\text{N}_2\cdot\text{Eu}$ and the like. The present oxynitride phosphor can adjust the color tone and brightness by changing a ratio of O to N in like manner as Embodiment 1. Further, the luminescence spectrum and intensity can be finely adjusted also by changing a molar ratio of cation to anion which is shown by $(L + M)/(O + N)$. This can be carried out, for example, by carrying out treatment such as vacuum and removing N and O, but the present invention is not limited to these processes. In the composition of the oxynitride phosphor, there may be contained at least one or more of Li, Na, K, Rb, Cs, Mn, Re, Cu, Ag and Au. The brightness and luminescence efficiency such as quantum efficiency can be adjusted by adding these. Further, other elements may be contained so far as the properties are not damaged.

[0062]

L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn in which Ba is essential. Namely, Ba may be used alone, but various combinations such as Ba and Ca, Ba and Sr, and Ba, Ca and Sr can be changed. The mixture of Group II elements can vary the compounding ratio, if necessary.

[0063]

M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf in which Si is essential. M may also use Si as a single body, and can change various combinations such as Si and Ge, and Si and C. Because the phosphor having good crystallinity and low cost can be provided using Si.

[0064]

R is one or more of the rare earth elements in which Eu is essential. Specifically, the rare earth elements are La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Eu may be used alone among these rare earth elements, but those containing Eu and at least one or more of elements selected from the rare earth elements can be also used. Because elements other than Eu act as a co-activator. As R, Eu is preferably contained by 70% by weight or more. In particular, R is a molar ratio of Group II element : R = 1 : 0.005 to 1 : 0.15.

[0065]

Europium Eu being the rare earth element is used as a luminescence center. The present invention is illustrated using only Eu, but is not limited to this, and those which were co-augmented with Eu can be used. Europium has mainly a divalent and trivalent energy levels. The phosphor of the present invention uses Eu^{2+} as the activator for an alkali earth metal silicone nitride being the mother body. Eu^{2+} is easily oxidized and commercially available as the composition of trivalent Eu_2O_3 in general.

[0066]

L and M of the main components can be also used as compounds thereof as the mother material. These L and M of the main components can be used as metals, oxides, imides, amides, nitrides, and various salts. Further, the elements of L and M of the main components may be preliminarily mixed to be used.

[0067]

Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. Q is also used as metals, oxides, imides, amides, nitrides, and various

salts. For example, they are B_2O_6 , H_3BO_3 , Al_2O_3 , $Al(NO_3)_3 \cdot 9H_2O$, AlN , $GaCl_3$, $InCl_3$ and the like.

[0068]

The nitride of L, the nitride of M and the oxide of M are mixed as the mother body materials. The oxide of Eu is mixed with said mother body materials as the activator. These are weighed so as to be the desired phosphor composition, and mixed until being homogeneous. In particular, the nitride of L, the nitride of M and the oxide of M in the mother body materials are preferably mixed at molar ratios of $0.5 < \text{the nitride of L} < 1.5$, $0.25 < \text{the nitride of M} < 1.75$, and $2.25 < \text{the oxide of M} < 3.75$. Namely, the fixed amounts of these mother body materials are weighed and mixed so as to be the composition ratio of $L_xM_yO_zN_{((2/3)X+Y-(2/3)Z-\omega)} \cdot R$ or $L_xM_yQ_tO_zN_{((2/3)X+Y+T-(2/3)Z-\omega)} \cdot R$.

[0069]

(Production process of oxynitride phosphor)

Then, the production process of the oxynitride phosphor, $BaSi_2O_2N_2 \cdot Eu$ related to the present invention is illustrated, but the present invention is not limited to the production processes below. Fig. 3 is a process chart showing the production process of the oxynitride phosphor.

[0070]

A nitride of Ba, a nitride of Si, an oxide of Si and an oxide of Eu are mixed according to predetermined ratios.

[0071]

Firstly, in the present process, the nitride of Ba, the nitride of Si, the oxide of Si and the oxide of Eu are prepared. As these raw materials, those purified are preferably used, but those commercially available may be used. The oxynitride phosphor is produced by following method.

[0072]

Ba_3N_2 is used as the nitride of Ba of a raw material. The single body of Ba preferably is used, but compounds such as an imide compound, an amide compound and

BaO can be also used as the raw material, and the single body of Ba can be also used.

Further, the Ba of a raw material may be those containing B, Ga and the like.

[0073]

The nitride of Ba, Ba_3N_2 , is crushed (P1). The crushing of the Ba of a raw material is carried out in a globe box in argon atmosphere or in nitride atmosphere.

[0074]

Si_3N_4 is used as the nitride of Si of a raw material. The single body of Si preferably is used, but as the raw material, a nitride compound, an imide compound, an amide compound and the like can be also used. For example, they are Si_3N_4 , $\text{Si}(\text{NH}_2)_2$, Mg_2Si , Ca_2Si , SiC and the like. The purity of the Si of a raw material is preferably 3N or more, but B, Ga and the like may be contained.

[0075]

The nitride of Si, Si_3N_4 , is crushed (P2). The crushing of the Si of a raw material is carried out in a globe box in argon atmosphere or in nitride atmosphere.

[0076]

SiO_2 is used as the oxide of Si of a raw material. Hereat, those which are commercially available are used (Silicon Dioxide 99.9%, 190-09072, manufactured by Wako Pure Chemicals Industries, Ltd.).

[0077]

The oxide of Si, SiO_2 , is crushed (P3).

[0078]

] Eu_2O_3 is used as the oxide of Eu of a raw material. The single body of Eu preferably is used, but as the raw material, a nitride compound, an imide compound, an amide compound and the like can be also used. Europium nitride other than europium oxide is preferably used. Because oxygen or nitrogen is contained in a product.

[0079]

The oxide of Eu, Eu_2O_3 , is crushed (P4).

[0080]

The above-mentioned nitride of Ba, Ba_3N_2 , which was crushed, the nitride of Si, Si_3N_4 , the oxide of Si, SiO_2 , and the oxide of Eu, Eu_2O_3 are weighed and mixed (P5). The above-mentioned raw materials are weighed so as to be a fixed compounding ratio.

[0081]

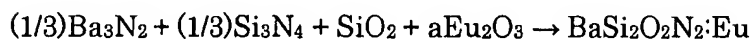
Then, the mixture of the nitride of Ba, the nitride of Si, the oxide of Si, and the oxide of Eu is calcined (P6). Said mixture is charged in a crucible to be calcined.

[0082]

The oxynitride phosphor represented by $\text{BaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ can be obtained by mixing and calcination (P7). The reaction formula of the basic constituting elements by the calcination is shown in Formula 1.

[0083]

[Formula 1]



However, the composition is a typical composition deduced from the compounding ratio, and has adequate properties which are worthwhile for practical use, around the ratio. Further, the composition of the objective phosphors can be changed by changing the compounding ratio of the respective raw materials.

[0084]

The calcination temperature is not specifically limited. The calcination is preferably carried out at a temperature of 1200 to 1700°C, and a calcination temperature of 1400 to 1700°C is more preferable. It is preferable to carry out the calcination of the raw materials of the phosphor 11 using a crucible made of boron nitride (BN) material and a boat. A crucible made of alumina (Al_2O_3) material can be also used in addition to the crucible made of boron nitride material.

[0085]

Further, the calcination is preferably carried out in reductive atmosphere. The reductive atmosphere is inactive gas atmospheres such as nitrogen atmosphere, nitrogen-hydrogen atmosphere, ammonia atmosphere and argon atmosphere, etc.

[0086]

The objective oxynitride phosphor can be obtained by using the above production process.

[0087]

Further, the oxynitride phosphor represented by $Ba_xSi_yB_zO_zN_{((2/3)X+Y+T-(2/3)Z-\omega)} \cdot Eu$ can be produced as below.

[0088]

An Eu oxide is preliminarily mixed with a B compound, H_3BO_3 in dry condition. Europium oxide is used as the Eu compound, but metal europium, europium nitride and the like can be also used in like manner as the fore-mentioned other constitution elements. Additionally, an imide compound, an amide compound and the like can be used as the Eu compound. Europium oxide is preferably those having high purity, but those commercially available can be also used. A B compound is mixed in a dry process but a wet mixing can be also carried out. Since these compounds are easily oxide, the crushing of the compounds is carried out in a globe box in argon atmosphere or in nitride atmosphere.

[0089]

The production process of the oxynitride phosphor is illustrated exemplifying the B compound H_3BO_3 . However, there are Li, K, Na and the like as the component constituting elements other than B, and as these compounds, for example, there can be used $LiOH \cdot H_2O$, Na_2CO_3 , K_2CO_3 , $RbCl$, $CsCl$, $Mg(NO_3)_2$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, $TiOSO_4 \cdot H_2O$, $ZrO(NO_3)_2$, $HfCl_4$, MnO_2 , $ReCl_5$, $Cu(CH_3COO)_2 \cdot H_2O$, $AgNO_3$, $HAuCl_4 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, GeO_2 , $Sn(CH_3COO)_2$ and the like.

[0090]

A mixture of Eu and B is crushed. The mean particle diameter of the mixture of Eu and B after the crushing is preferably about $0.1\mu m$ to $15\mu m$.

[0091]

After the above-mentioned crushing, the nitride of Ba, the nitride of Si, the oxide of Si, and the oxide of Eu containing B are mixed in like manner as the fore-mentioned

production steps of $\text{BaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$. After said mixing, calcination is carried out and the objective oxynitride phosphor can be obtained.

[0092]

(Second phosphor 11, 108)

A second phosphor is contained in the phosphor 11, 108 together with the oxynitride phosphor. The second phosphor is preferably at least one or more selected from an alkali earth halogen apatite phosphor, an alkali earth metal borate halogen phosphor, an alkali earth metal aluminate phosphor, an alkali earth silicate, an alkali earth sulfide, an alkali earth thiogallate, an alkali earth silicone nitride, and a germanic acid salt which are mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn; or a rare earth aluminate and a rare earth silicate which are mainly activated by the Lanthanide series element such as Ce; an organic and organic complex which are mainly activated by elements such as the Lanthanide series element such as Eu. As the specific example, phosphors below can be mentioned, but the present invention is not limited to these.

[0093]

As the alkali earth halogen apatite phosphor which is mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn, there are $\text{M}_5(\text{PO}_4)_3\text{X}\cdot\text{R}$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I. R is at least one or more of Eu, Mn, and Eu and Mn.) and the like.

[0094]

As the alkali earth metal borate halogen phosphor, there are $\text{M}_2\text{B}_5\text{O}_9\text{X}\cdot\text{R}$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I. R is at least one or more of Eu, Mn, and Eu and Mn.) and the like.

[0095]

As the alkali earth metal aluminate phosphor, there are $\text{SrAl}_2\text{O}_4\cdot\text{R}$, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}\cdot\text{R}$, $\text{CaAl}_2\text{O}_4\cdot\text{R}$, $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}\cdot\text{R}$, $\text{BaMg}_2\text{Al}_{16}\text{O}_{12}\cdot\text{R}$, $\text{BaMgAl}_{10}\text{O}_{17}\cdot\text{R}$ (R is at least one or more of

Eu, Mn, and Eu and Mn.) and the like.

[0096]

As the alkali earth sulfide phosphor, there are $\text{La}_2\text{O}_2\text{S}:\text{Eu}$, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$, $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}$ and the like.

[0097]

As the rare earth aluminate phosphor which is mainly activated by the Lanthanide series element such as Ce, there are YAG-base phosphors represented by the composition formulae of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, $(\text{Y}_{0.8}\text{Gd}_{0.2})_3\text{Al}_5\text{O}_{12}:\text{Ce}$, $\text{Y}_3(\text{Al}_{0.8}\text{Ga}_{0.2})_5\text{O}_{12}:\text{Ce}$ and $(\text{Y}, \text{Gd})_3(\text{Al}, \text{Ga})_5\text{O}_{12}:\text{Ce}$ and the like.

[0098]

As other phosphors, there are $\text{ZnS}:\text{Eu}$, $\text{Zn}_2\text{GeO}_4:\text{Mn}$, $\text{MGe}_2\text{S}_4:\text{Eu}$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I.) and the like. Further, there are also $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}$, $\text{MSi}_7\text{N}_{10}:\text{Eu}$, $\text{M}_{1.8}\text{Si}_5\text{O}_{0.2}\text{N}_8:\text{Eu}$, $\text{M}_{0.9}\text{Si}_7\text{O}_{0.1}\text{N}_{10}:\text{Eu}$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn.) and the like.

[0099]

The above-mentioned second phosphor can contain one or more selected from Tb, Cu, Ag, Au, Cr, Nd, Dy, Co, Ni and Ti, in place of Eu, or in addition to Eu if necessary.

[0100]

Further, phosphors other than the above-mentioned phosphors which have the similar performances and effects can be also used.

[0101]

As these second phosphors, there can be used phosphors which have luminescence spectra at a red color, a green color and a blue color by the excitation light of the light-emitting elements 10 and 101, and additionally, there can be also used phosphors which have luminescence spectra at a yellow color, a blue green color and an orange color which are intermediate colors. There can be produced the light-emitting device having various luminescence colors by using these second phosphors in combination with the first

phosphor.

[0102]

For example, there can be provided the light-emitting device with good color rendering which emits white light by using the phosphors 11 and 108 comprising $\text{CaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ or $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}$ being the first phosphor which emits green to yellow light, $(\text{Sr}, \text{Ca})_5(\text{PO}_4)_3\text{Cl:Eu}$ being the second phosphor which emits blue light, and $(\text{Ca}, \text{Sr})_2\text{Si}_5\text{N}_8\text{:Eu}$. Because red, blue and green which are three primary colors of color are used, therefore a desired white light can be realized only by changing the compounding ratio of the first phosphor and the second phosphor. In particular, when light nearby 460nm as an excitation light source is irradiated to the oxynitride phosphor and the second phosphor, the oxynitride phosphor emits light around 500nm. There can be provided the white color light-emitting device with good color rendering, thereby.

[0103]

The particle diameter of the above-mentioned phosphors 11 and 108 is preferably 1 μm to 20 μm , more preferably 2 μm to 8 μm , and preferably 5 μm to 8 μm in particular. A phosphor having a particle diameter of 2 μm or less is apt to form aggregates. On the other hand, a phosphor having a particle diameter of 5 μm to 8 μm has the high absorption rate and conversion efficiency of light. Thus, the mass productivity of the light-emitting device is improved by containing the phosphors having a large particle diameter which have optically superior properties.

[0104]

Wherein the particle diameter means the mean particle diameter obtained by an air transmission process. Specifically, a sample by 1 cm^3 is weighed under environments of a temperature of 25°C and a humidity of 70% and packed in an exclusive use tubular container, then dry air at fixed pressure is flown, and a specific surface area is read from differential pressure to obtain a value converted to the mean particle diameter. The mean particle diameter of the phosphors used in the present invention is preferably 2 μm to 8 μm . Further, the phosphor having the value of the mean particle diameter is preferably

contained in high frequency. Further, those whose particle size distribution is narrow are preferable, and those having fine particles with 2 μ m or less are preferable in particular. Thus, the light-emitting device suppressing color unevenness and having good color tone is obtained by using phosphors having the little unevenness of the particle diameter and particle size distribution.

[0105]

The position of arranging the phosphor 108 in the light-emitting device of Fig. 2 can be arranged at various positions in the positional relation with the light-emitting element 101. For example, the phosphor 108 can be contained in a mold material coating the light-emitting element 101. Further, the light-emitting element 101 and the phosphor 108 may be arranged at an interval, and the phosphor 108 may be directly mounted on the upper part of the light-emitting element 101.

[0106]

(Coating member 12, 109)

The phosphor 11, 108 can be adhered using various coating members (binder) such as the resins of organic materials and glass of inorganic materials. The coating member 12 has occasionally a role as a binder for fixing the phosphor 11 on the light-emitting element 10, the window portion 107 and the like. When an organic substance is used as the coating member (binder), as the specific material, there are preferably used transparent resins excellent in weather resistance such as an epoxy resin, an acryl resin and a silicone resin. When a silicone is used, it is preferable because it is superior in reliability and the dispersibility of the phosphor 11 can be improved.

[0107]

Further, when an inorganic substance having the similar thermal expansion coefficient as the window portion 107 is used as the coating member 12 (binder), it is preferable because the phosphor 108 can be adhered on the fore-mentioned window portion 107. As the specific processes, there can be used a sedimentation process, a sol-gel process, a spray process and the like. For example, silanol ($\text{Si}(\text{OEt})_3\text{OH}$) and ethanol are

mixed with the phosphors 11 and 108 to form a slurry, the slurry is vomited from a nozzle, then the mixture is heated at 300°C for 3 hours to convert silanol into SiO₂, and the phosphor can be fixed on a desired position.

[0108]

Further, the binding agent being an inorganic substance can be also used as the coating members (binder) 12 and 109. The binding agent is a so-called low melting point glass and fine particles, and preferably absorbs little radiation at an ultraviolet to visible region and is extremely stable in the coating members (binders) 12 and 109.

[0109]

When the phosphor having large particle diameters is adhered with the coating members (binders) 12 and 109, there are preferably used binding agents in which particles are ultra fine powder even if its melting point is high, such as for example, silica sol, alumina, or alkali earth metal pyrophosphate and phosphate having a fine particle size which is obtained by a sedimentation process. These binding agents can be used alone or they are mutually mixed to be used.

[0110]

Hereat, the coating process of the above-mentioned binding agent is described. In order to sufficiently enhance binding effect, the binding agent is preferably crushing in a vehicle in wet condition to prepare a slurry, and used as a binding agent slurry. The fore-mentioned vehicle is a highly viscous solution which is obtained by dissolving a small amount of an adhesive binding agent in an organic solvent or deionized water. For example, an organic-base vehicle is obtained by containing 1% by weight of nitrocellulose being the adhesive binding agent based on butyl acetate being an organic solvent.

[0111]

The phosphors 11 and 108 are contained in the binding agent slurry thus obtained to prepare a coating solution. As the addition amount of the slurry in the coating solution, the total amount of the binding agent in the slurry can be 1 to 3% by weight based on the phosphor amount in the coating solution. It is preferable that the addition amount of the

binding agent is little in order to suppress the lowering of a beam retention rate.

[0112]

The fore-mentioned coating solution is coated on the back face of the fore-mentioned window portion 107. Then, warm wind or hot wind is blown to dry it. Finally, baking is carried out at a temperature of 400°C to 700°C to disperse the fore-mentioned vehicle. Thus, the phosphor layer is adhered on a desired position with the binding agent.

[0113]

(Light-emitting element 10, 101)

The light-emitting element 10, 101 is preferably a semiconductor light-emitting element having a luminescent layer which emits light with a wavelength which can excite the oxynitride phosphor efficiently. As the material of the semiconductor light-emitting element, there can be mentioned various semiconductors such as BN, SiC, ZnSe, GaN, InGaN, InAlGaN, AlGaN, BaGaN and BInAlGaN. Further, a luminescence center can be also made by containing Si, Zn and the like in these elements as impurity elements. As the semiconductor material which can efficiently emit light at a short wavelength region among an ultraviolet region and a visible light region which can efficiently excite the phosphor 11 (oxynitride phosphor), there can be preferably mentioned nitride semiconductors (for example, a nitride semiconductor containing Al and Ga, $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$, $0 \leq x$, $0 \leq y$, $x+y \leq 1$ as a nitride semiconductor containing In and Ga).

[0114]

Further, as the structure of the semiconductor light-emitting element, there are preferably mentioned semiconductors having a homo structure, a hetero structure or a double hetero structure having an MIS junction, a PIN junction, a p-n junction and the like. A luminescence wavelength can be variously selected by the material of semiconductor layers and mix crystal ratio. Further, output power can be also further improved by making a single quantum well structure and a multi quantum well structure in which a

semiconductor activating layer was formed to be a thin film which generates quantum effect.

[0115]

When the light-emitting element 10 is composed of the nitride semiconductor, there are preferably used a substrate comprising materials such as sapphire, spinel, SiC, Si, ZnO, GaAs and GaN. The sapphire substrate is preferably used for forming the nitride semiconductor having good crystallinity by mass production. The nitride semiconductor can be formed on the sapphire substrate using a HVPE process, a MOCVD process and the like. Specifically, an amorphous buffer layer in which GaN, AlN, GaAlN and the like were grown at a low temperature is formed on the sapphire substrate, and the nitride semiconductor having a p-n junction is formed thereon.

[0116]

The preparation example of the light-emitting element capable of efficiently emitting light at an ultraviolet region which has a p-n junction using the nitride semiconductor is as below. Firstly, SiO₂ is formed in a stripe form about perpendicular to an orientation flat face of a sapphire substrate on the buffer layer. Then, ELOG (Epitaxial Lateral Over Grows GaN) growth of GaN is carried out on it using an HVPE process. Successively, the first contact layer formed with n-GaN, the first clad layer formed with n-AlGa_{0.3}N, active layers having a multi quantum well structure which laminated a plural number of layers of the well layers of InAlGa_{0.3}N and the barrier layers of AlGa_{0.3}N, the second clad layer formed with p-AlGa_{0.3}N, and the second contact layer formed with p-GaN are laminated in order by the MOCVD process. Thus, the nitride semiconductor light-emitting element having a double hetero structure is prepared. Further, the semiconductor laser element which can be utilized for the present invention can be prepared by making the active layer be ridge stripe form, sandwiching it with guide layers, and providing the edge face of a resonator.

[0117]

Further, the nitride semiconductor exhibits an n-type conductivity in a condition

in which impurities are not doped, but Si, Ge, Se, Te, C and the like are appropriately introduced as an n-type dopants in order to form an n-type nitride semiconductor having a desired carrier levels for purposes of improving the luminescence efficiency and the like. On the other hand, when a p-type nitride semiconductor is formed, Zn, Mg, Be, Ca, Sr, Ba and the like which are p-type dopants are preferably doped. Further, since the nitride semiconductor is hardly converted to p-type only by doping the p-type dopants, it is preferable to lower the resistance by heating with a furnace, plasma irradiation and the like after introducing the p-type dopants. When the sapphire substrate is not removed, the portion of the first contact layer is exposed by etching from a p-type side to the surface of the first contact layer, and electrodes are respectively formed on the respective contact layers. Then, the light-emitting elements comprising the nitride semiconductor are prepared by cutting in a chip shape from the semiconductor wafer.

[0118]

When the phosphor 11, 108 is fixed around the surface of the light-emitting element 10, 101 in the light-emitting device of the present invention, a resin is preferably utilized for forming in good mass productivity. In this case, when both of the relation with the luminescence wavelength of the phosphor 11, 108 and the deterioration protection of the transparent resin are considered, the light-emitting element 10, 101 having a luminescence spectrum at an ultraviolet region, whose luminescence peak wavelength is 360nm or more and 420nm or less, or 450nm or more and 470nm or less, is preferably used.

[0119]

Hereat, the semiconductor light-emitting element 10 used in Embodiment 2 is preferably adjusted so that the sheet resistance R_n of an n-type contact layer in which impurity levels are 10^{17} to $10^{20}/\text{cm}^3$ and the sheet resistance R_p of a transparent p-type electrode become the relation of the sheet resistance of $R_p \geq R_n$. The n-type contact layer is preferably formed at a film thickness of 3 to $10\mu\text{m}$ and more preferably 4 to $6\mu\text{m}$, and the sheet resistance R_n is estimated to be 10 to $15\Omega/\square$. Accordingly, it is preferable to set the thickness so that the sheet resistance R_p of the transparent p-type electrode is 10 to

15Ω/□. Specifically, the transparent p-type electrode may be formed at a thin film thickness of 150μm or less.

[0120]

Further, when the transparent p-electrode is formed by one kind selected from a group of gold and platinum and a multilayered film or alloy comprising at least one kind of other elements, stability and reproducibility are improved by adjusting the sheet resistance of the transparent p-electrode by the content of gold or platinum element contained. Since gold or a metal element has a high absorption coefficient at the wavelength of the semiconductor light-emitting element used for the present invention, the lesser the amount of gold or platinum element contained in the transparent p-electrode is, the better the transparency is. A conventional semiconductor light-emitting element had the relation of the sheet resistance of $R_p \leq R_n$, but since it is $R_p \geq R_n$ in Embodiment 2, the transparent p-electrode is formed in a thinner film in comparison with a conventional one. The thin film forming can be easily attained by reducing the amount of gold or platinum element.

[0121]

As described above, the semiconductor light-emitting element used for the present invention has preferably the relation of $R_p \geq R_n$ for the sheet resistance $R_n\Omega/\square$ of n-contact layer and the sheet resistance $R_n\Omega/\square$ of the transparent p-electrode. However, since it is difficult to measure R_n after preparing the semiconductor light-emitting element 10, it is substantially impossible to know the relation of R_p and R_n , but it is possible to know what relation exists between R_p and R_n from the condition of light intensity distribution at light emission.

[0122]

When the transparent p-electrode and n-contact layer have the relation of $R_p \geq R_n$, it is preferable to provide a p-side pedestal electrode having an extended conduction portion in contact with the fore-mentioned transparent p-electrode, therefore the external quantum efficiency can be further improved. The shape and direction of the extended

conduction portion is not limited, and when the extended conduction portion is a linear shape, an area obstructing light is preferably reduced, but the shape may be a mesh shape. The shape may be a curve, a lattice, a branch and a hook other than the linear shape. Hereat, since the shading effect is increased in proportion to the total area of the p-side pedestal electrode, it is preferable to design the line width and length of the extended conduction portion so that the shading effect does not exceeds the luminescence increasing effect.

[0123]

(Light emitting element 10, 101)

As described above, not only a light-emitting element emitting ultraviolet light, but also a light-emitting element emitting blue light can be also used as the light-emitting element 10, 101. The light-emitting element 10, 101 emitting blue light is also preferably Group III nitride compound light-emitting element. For example, such light-emitting element 10 has a laminated structure in which an Si undoped n-GaN layer, an n-contact layer comprising Si-doped n-GaN, an undoped n-GaN layer, a luminescent layer having a multi quantum well structure(the multi quantum well structure of GaN barrier layer/InGaN well layer), a p-clad layer comprising Mg-doped p-GaN, and a p-contact layer comprising Mg-doped p-GaN are laminated in order on a sapphire substrate through GaN buffer layer. Further, electrodes are formed as below. Provided that the light-emitting elements different from the constitution can be also used.

[0124]

A p-Ohmic electrode is formed almost all over the surface on the p-contact layer, and a p-pad electrode is formed on the portion of the p-ohmic electrode.

[0125]

Further, the undoped GaN layer is removed from the p-contact layer by etching, the portion of the n-contact layer is exposed, and the n-electrode is formed on the exposed portion.

[0126]

Further, the luminescent layer having a multi quantum well structure was used in Embodiment, but the present invention is not limited to this. For example, it may be a single quantum well structure utilizing InGaN, and GaN to which Si, Zn and the like were doped may be utilized.

[0127]

Further, in the luminescent layer of the light-emitting element 10, 101, the main luminescence peak wavelength can be varied within a range of 420nm to 490nm by changing the content of In. Further, the luminescence peak wavelength is not limited to the above-mentioned range, and those having the luminescence peak wavelength the luminescence peak wavelength at 360 to 550nm can be also used.

[0128]

(Coating member 12, 109)

The coating member 12 (transparent material) is provided in the cup of the lead frames 13, and used by being mixed with the phosphor 11. As the specific material of the coating member 12, there are used transparent resins excellent in temperature property and weather resistance such as an epoxy resin, a urea resin and a silicone resin; silica sol, glass, an inorganic binder and the like. Further, a dispersant, barium titanate, titanium oxide, aluminum oxide and the like may be contained together with the phosphor.

Further, a light stabilizer and a coloring agent may be contained.

[0129]

(Lead frame 13)

The lead frame 13 is constituted by the mount lead 13a and the inner lead 13b.

[0130]

The mount lead 13a arranges the light-emitting element 10. The upper part of the mount lead 13a is a cup shape, and the light-emitting element 10 is die-bonded in the cup. The light-emitting element 10 is covered in the cup with the fore-mentioned phosphor 11 and the fore-mentioned coating member 12. Further, a plural number of the light-emitting elements 10 are arranged in the cup, and the mount lead 13a can be utilized

as a common electrode of the plural number of the light-emitting elements 10. In this case, an adequate electroconductivity and the connecting property of the electroconductive wire 14 are required. The die bonding (adhesion) of the light-emitting element 10 with the cup of the mount lead 13a can be carried out by a thermosetting resin and the like. As the thermosetting resin, an epoxy resin, an acryl resin, an imide resin and the like are mentioned. Further, it is die-bonded with the mount lead 13a by the face down light-emitting element 10 and the like, and an Ag paste, a carbon paste, a metal bump and the like can be used for carrying out electric connection. Further, an inorganic binder can be also used.

[0131]

The inner lead 13b is electrically connected with the electroconductive wire 14 which is extended from the electrode 3 of the light-emitting elements 10 which were arranged on the mount lead 13a. The inner lead 13b is preferably arranged at a position which is separated from the mount lead 13a for preventing a short circuit with the mount lead 13a. When a plural number of the light-emitting elements 10 are arranged on the mount lead 13a, a constitution in which the respective wires are not mutually connected is required. The inner lead 13b uses preferably the similar material as that of the mount lead 13a, and iron, copper, copper with iron, gold, platinum, silver and the like can be used.

[0132]

(Electroconductive wire)

The electroconductive wire 14 connects electrically the electrode 3 of the light-emitting elements 10 with the lead frame 13. The electroconductive wire 14 is preferably those having good ohmic property, mechanical connecting property and heat conductivity with the electrode 3. The specific material of the electroconductive wire 14 is preferably metals such as gold, copper, platinum, aluminum and the like, and alloys thereof, etc.

[0133]

(Mold member)

The mold member 15 is provided for protecting the light-emitting elements 10, the phosphor 11, the coating member 12, the lead frame 13, the electroconductive wire 14 and the like from the external. The mold member 15 has purposes of expanding the angle of visibility, reducing the directionality from the light-emitting elements 10, and focusing and scattering luminescence in addition to the purpose of protection from the external. In order to attain the purposes, the mold member can be formed in a desired shape. Further, the mold member 15 may be a convex lens shape, a concave lens shape, additionally, a structure in which a plural number of layers were laminated. As the specific material of the mold member 15, there can be used materials excellent in transmission property, weather resistance and temperature property such as an epoxy resin, a urea resin, a silicone resin, a silica sol, a glass, and the like. A dispersant, a coloring agent, an ultraviolet absorbent and a phosphor be contained in the mold member 15. As the dispersant, barium titanate, titanium oxide, aluminum oxide and the like are preferable. The same material is preferably used for reducing the repulsion of the coating member 12 with the material and for considering a refractive index.

[0134]

The phosphors and the light-emitting device related to the present invention are illustrated below according to examples, but not limited to these examples.

[0135]

Further, temperature properties are shown by a relative brightness in which the luminescence brightness at 25°C is 100%. Further, the particle diameter shows the fore-mentioned particle diameter, and is a value obtained by an air transmission process called as F.S.S.No. (Fisher Sub Sieve Sizer's No.).

[0136]

[EXAMPLE]

The Examples of the present invention will be described below.

[0137]

(Phosphor)

Fig. 4 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $\lambda_{\text{ex}} = 400\text{nm}$. Fig. 5 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $\lambda_{\text{ex}} = 460\text{nm}$. Fig. 6 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 7 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 8 is an SEM photo photographing the oxynitride phosphor of Example 1. Fig. 8(a) is an SEM photo photographed at a magnification of 1000-fold, and Fig. 8(b) is an SEM photo photographed at a magnification of 5000-fold.

[0138]

In Examples 1 to 5, the portion of Ba is substituted with Eu, and said Eu concentration is changed. Example 1 is $\text{Ba}_{0.97}\text{Eu}_{0.03}\text{Si}_2\text{O}_2\text{N}_2$. Example 2 is $\text{Ba}_{0.95}\text{Eu}_{0.05}\text{Si}_2\text{O}_2\text{N}_2$. Example 3 is $\text{Ba}_{0.90}\text{Eu}_{0.10}\text{Si}_2\text{O}_2\text{N}_2$. Example 4 is $\text{Ba}_{0.85}\text{Eu}_{0.15}\text{Si}_2\text{O}_2\text{N}_2$. Example 5 is $\text{Ba}_{0.80}\text{Eu}_{0.20}\text{Si}_2\text{O}_2\text{N}_2$.

[0139]

Firstly, Ba_3N_2 , Si_3N_4 , SiO_2 and Eu_2O_3 were used as the raw materials. Said raw materials were crushed at 0.1 to $3.0\mu\text{m}$. Example 1 used the under-mentioned amounts of the raw materials so as to be the above-mentioned composition after crushing. Wherein a molar ratio of Eu to Ba is $\text{Ba} : \text{Eu} = 0.97 : 0.03$.

Ba_3N_2 : 5.60 g

Si_3N_4 : 1.88 g

SiO_2 : 2.31 g

Eu_2O_3 : 0.21 g

After weighing the above-mentioned amounts, Ba_3N_2 , Si_3N_4 , SiO_2 and Eu_2O_3 were mixed until uniformity.

[0140]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1500°C for about 5 hours.

[0141]

The objective oxynitride phosphor was obtained thereby. The theoretical composition of the oxynitride phosphor obtained is $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$.

[0142]

When the % by weight of O and N in the oxynitride phosphor of Example 1 was measured, O and N were contained by 12.1% by weight and 8.9% by weight respectively. The weight ratio of O to N is $\text{O} : \text{N} = 1 : 0.74$.

[0143]

The calcination of the oxynitride phosphor related to Examples is carried out in ammonia atmosphere using a boron nitride crucible. A crucible made of a metal is not preferably used for the crucible. When the crucible made of a metal is used, it is considered that the crucible is eroded and it causes the lowering of luminescence properties. Accordingly, it is preferable to use a crucible made of ceramics such as alumina.

[0144]

Example 2 changes the compounding ratio of Eu. Example 2 is the oxynitride phosphor in which the portion of Ba was substituted with Eu. The under-mentioned amounts of crushed powders were weighed. Wherein a molar ratio of Eu to Ba is $\text{Ba} : \text{Eu} = 0.95 : 0.05$.

Ba_3N_2 : 5.48 g

Si_3N_4 : 1.91 g

SiO_2 : 2.28 g

Eu_2O_3 : 0.35 g

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0145]

Example 3 changes the compounding ratio of Eu. Example 3 is the oxynitride phosphor in which the portion of Ba was substituted with Eu. The under-mentioned amounts of crushed powders were weighed. Wherein a molar ratio of Eu to Ba is $\text{Ba} : \text{Eu}$

= 0.90 : 0.10.

Ba₃N₂ : 5.18 g

Si₃N₄ : 1.97 g

SiO₂ : 2.18 g

Eu₂O₃ : 0.69 g

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0146]

Example 4 changes the compounding ratio of Eu. Example 4 is the oxynitride phosphor in which the portion of Ba was substituted with Eu. The under-mentioned amounts of crushed powders were weighed. Wherein a molar ratio of Eu to Ba is Ba : Eu = 0.85 : 0.15.

Ba₃N₂ : 4.87 g

Si₃N₄ : 2.03 g

SiO₂ : 2.09 g

Eu₂O₃ : 1.03 g

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0147]

Example 5 changes the compounding ratio of Eu. Example 5 is the oxynitride phosphor in which the portion of Ba was substituted with Eu. The under-mentioned amounts of crushed powders were weighed. Wherein a molar ratio of Eu to Ba is Ba : Eu = 0.80 : 0.20.

Ba₃N₂ : 4.57 g

Si₃N₄ : 2.10 g

SiO₂ : 1.99 g

Eu₂O₃ : 1.37 g

Said raw materials were mixed and calcination was carried out under the same

conditions as Example 1.

[0148]

Any of the calcined products of Examples 1 to 5 is crystalline powder or particles.

The particle diameter was about 1 to 5 μ m.

[0149]

Table 1 shows the luminescence properties when the oxynitride phosphors of Examples 1 to 5 were excited by Ex = 400nm.

Table 1

	Eu concentration (mol)	Color tone x	Color tone y	Luminescence brightness (%)	Quantum efficiency (%)	Luminescence peak wavelength (nm)
Example 1	0.03	0.106	0.471	100.0	100.0	496
Example 2	0.05	0.121	0.481	85.5	83.9	498
Example 3	0.10	0.247	0.477	45.2	40.1	500
Example 4	0.15	0.289	0.556	33.4	22.8	504
Example 5	0.20	0.317	0.599	23.0	13.7	536

The measurement of the excitation spectra of the oxynitride phosphors of Examples 1 to 5 was carried out. As a result of the measurement, Examples 1 to 4 are more strongly excited at from 370nm to 470nm than nearby 350nm.

[0151]

The measurement of the reflection spectra of the oxynitride phosphors of Examples 1 to 5 was carried out. As a result of the measurement, Examples 1 to 5 exhibit high absorption rate at from 290nm to 470nm. Accordingly, they absorb efficiently light from the excitation light source from 290nm to 470nm and can carry out wavelength conversion.

[0152]

Light nearby Ex = 400nm as the excitation light source was irradiated to the oxynitride phosphors of Examples 1 to 5 to be excited. The oxynitride phosphor of Example 1 has a luminescence color at a green region of the color tone, x = 0.106 and the

color tone $y = 0.471$, and the luminescence peak wavelength $\lambda_p = 496\text{nm}$. The oxynitride phosphor of Example 2 has a luminescence color at a green region of the color tone, $x = 0.121$ and the color tone $y = 0.481$, and $\lambda_p = 498\text{nm}$. The oxynitride phosphor of Example 3 has a luminescence color at a green region of the color tone, $x = 0.247$ and the color tone $y = 0.477$, and $\lambda_p = 500\text{nm}$. Any of the oxynitride phosphors of Examples 1 to 3 exhibited higher luminescence efficiency than a conventional phosphor. In particular, the oxynitride phosphors of Examples 1 to 4 exhibited higher luminescence efficiency than Example 5. Further, Examples 2 to 5 are represented by the relative value on the basis that the luminescence brightness and quantum efficiency of Example 1 is 100%.

[0153]

Table 2 shows the temperature properties of the oxynitride phosphor of Example 1. The temperature properties are shown by the relative brightness on the basis that the luminescence brightness at 25°C is 100%. The excitation light source is light nearby $\text{Ex} = 400\text{nm}$.

[0154]

Table 2

Temperature ($^\circ\text{C}$)	Luminescence brightness (%)	Quantum efficiency (%)
25	100.0	100.0
50	97.0	97.4
100	88.8	90.2
150	79.2	81.7
200	64.7	68.2

As a result, when the oxynitride phosphor was raised to 100°C , it was 88.8% and keeps extremely high luminescence brightness, and even if the temperature was further raised to 200°C , it is 64.7% and keeps extremely high luminescence brightness. The oxynitride phosphor exhibits extremely good temperature properties.

[0155]

When the X-ray diffraction images of the above-mentioned these oxynitride

phosphors were measured, any image shows a sharp diffraction peak, and it was cleared that the phosphors obtained were crystalline compounds having regularity.

[0156]

<Light-emitting device>

The light-emitting device of Example 1 was produced using the above-mentioned oxynitride phosphor. As the excitation light source, a light-emitting element having a luminescence spectrum of 400nm. As the phosphor, $\text{BaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ of Example 1, $(\text{Y}, \text{Gd})_3(\text{Al}, \text{Ga})_5\text{O}_{12}\cdot\text{Ce}$, $\text{SrCaSi}_5\text{N}_8\cdot\text{Eu}$ and $(\text{Ca}_{0.93}, \text{Eu}_{0.05}, \text{Mn}_{0.02})_{10}(\text{PO}_4)_6\text{Cl}_2$ are used. Fig. 1 shows the light-emitting device of the present invention. Fig. 9 is a plane view of the light emitting element of the present invention. Fig. 10 is a sectional view of the light emitting element of the present invention. Fig. 11 is a chart showing the luminescence spectrum (simulation) of the light-emitting device of Example 1. Fig. 12 is a chart showing the chromaticity coordinates (simulation) of the light-emitting devices of Examples 1 to 3. Said light-emitting device of Example 1 adjusts a color temperature at 4000 to 5000K.

[0157]

(Light-emitting element)

The substrate 201 comprising sapphire (c plane) was set in the reaction vessel of MOVPE, and the temperature of the substrate 201 was raised until about 1050°C while flowing hydrogen to clean the substrate 201.

[0158]

Wherein a sapphire substrate is used for the substrate 201 in the present Example, but there may be used different kind substrates different from a nitride semiconductor substrate, namely nitride semiconductor substrates such as AlN , AlGaN and GaN , as the substrate 201. As the different kind substrates, for example, there can be used insulating substrate such as sapphire in which either of a C plane, R plane and A plane is a main plane, and spinel (MgAl_2O_4); oxide substrates which lattice-coordinate with SiC (including 6H, 4H and 3C), ZnS , ZnO , GaAs , Si and a nitride semiconductor; substrate materials which can grow a nitride semiconductor and are different from the nitride

semiconductor. As the preferable different kind substrates, sapphire and spinel are mentioned. Further, the different kind substrates may be off-angled, and in this case, when a substrate which was off-angled in a stepwise shape is used, the growth of the groundwork layer 202 comprising GaN is grown in good crystallinity, therefore it is preferable. Further, when the different kind substrate is used, a nitride semiconductor which becomes the groundwork layer 202 before formation of element structure is grown on the different kind substrate, then the different kind substrate is removed by processes such as polishing, and an element structure may be formed as the single body substrate of the nitride semiconductor. Further, there may be a process of removing the different kind substrate after forming the element structure. The substrate of the nitride semiconductor such as AlN may be used in addition to a GaN substrate.

[0159]

(Buffer layer)

Successively, the temperature of the substrate 201 is lowered to 510°C, and a buffer layer (not illustrated) comprising GaN is grown on the substrate 201 at a film thickness of about 100 angstroms using hydrogen as a carrier gas and ammonia and TMG (trimethylgallium) as the raw material gases.

[0160]

(Groundwork layer)

After forming the buffer layer, only TMG is stopped, and the temperature of the substrate 201 is raised to 1050°C. When it reached at 1050°C, an undoped GaN layer is grown at a film thickness of 2µm similarly using ammonia gas and TMG as the raw material gases.

[0161]

(n-Type layer)

Successively, an n-type layer 203 comprising GaN in which Si was doped by $4.5 \times 10^{18}/\text{cm}^3$ is grown at a thickness of 3µm at 1050°C similarly using ammonia gas and TMG as the raw material gases and silane gas as impurity gas, as a n

n-side contact layer which forms the n-side electrode 211a as the n type layer.

[0162]

(Active layer)

A barrier layer comprising Si-doped GaN is grown at a film thickness of 50 angstroms, and successively, a well layer comprising undoped $\text{In}_{0.1}\text{Ga}_{0.7}\text{N}$ is grown at a film thickness of 50 angstroms at 800°C using TMG, TMI and ammonia. Then, 4 layers of the barrier layer and 3 layers of well layer are alternatively laminated in order of barrier + well + barrier + well + barrier, and the active layer 204 comprising a multiple quantum well structure having a total film thickness of 350 angstroms is grown.

[0163]

(p-Side carrier confining layer)

Then, the p-side carrier confining layer 205 comprising $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ in which Mg was doped by $5 \times 10^{19}/\text{cm}^3$ is grown at a film thickness of 100 angstroms using TMG, TMA, ammonia and Cp_2Mg (cyclopentadienylmagnesium).

[0164]

(The first p-layer)

Successively, the first p-layer 206 comprising GaN in which p-type impurities were doped is grown at a film thickness of 0.1 μm using TMG, ammonia and Cp_2Mg .

[0165]

(The second p-layer)

As the second p-layer, a p-side contact layer 208 on whose surface a p-side electrode 210 is formed is formed. The p-side contact layer 208 is obtained by growing a p-type GaN in which Mg was doped by $1 \times 10^{20}/\text{cm}^3$ on the current diffusion layer, at a film thickness of 150 angstroms. Since the p-side contact layer 208 is a layer on which the p-side electrode 210 is formed, it is preferably a high carrier concentration with $1 \times 10^{17}/\text{cm}^3$ or more. When it is lower than $1 \times 10^{17}/\text{cm}^3$, it is apt to be difficult to obtain a preferable contact with the electrode. Further, when the composition of the contact layer is GaN, it is easy to obtain a preferable contact with the electrode material.

[0166]

After completion of the reaction forming the above element structure, the temperature is lowered to room temperature, and annealing is carried out at 700°C charging a wafer in the reaction vessel under nitrogen atmosphere, and the resistance of the p-layer is further lowered. The wafer on which the element structure was formed is taken out from the equipment, and an electrode forming step described below is carried out.

[0167]

After the annealing, the wafer is taken out from the reaction vessel, a fixed mask is formed on the surface of the p-side contact layer 208 being the uppermost layer, etching is carried out from the p-side contact layer 208 side with an RIE (reactive ion etching) equipment to expose the surface of the n-side contact layer, and an electrode forming surface is formed.

[0168]

As a p-side electrode 210, Ni and Au are laminated in order, and the p-side contact layer comprising Ni/Au is formed. Further, the p-side electrode 210 becomes an ohmic electrode which is brought in contact with the second p-layer and the p-side contact layer 208. At this time, the electrode branch 210a formed has a width of the stripe shape luminescent portion 209 of about 5µm and a width of the stripe shape electrode branch 210 of about 3µm, and the stripe shape luminescent portion 209 and the stripe shape electrode branch 210 are alternately formed. Only the portion of the p-side electrode 210 is formed at a region where the p-pat electrode is formed, and formed over the p-pat electrode to be electrically conducted. At this time, only the portion of the p-side electrode 210 is formed at a region where the p-pat electrode is formed, the p-pat pat electrode 210b is formed on the surface of the p-side contact layer 208, the portion is formed over the p-side electrode 210 to be electrically conducted. At this time, there is obtained a structure in which the surface of the p-side contact layer 208 where the p-side pat electrode 210b is provided is not brought in contact with the p-side electrode 210 and the p-side contact layer 208, a shot

key barrier is formed between both, current does not directly run in the element from the forming portion of the p-side pat electrode 210b, and current is injected in the inside of the element through the electrode branch 210a which was electrically connected.

[0169]

Successively, an n-electrode 211a is formed on the exposed plane 203a on which the n-layer 203 was exposed. The n-electrode 211a is formed by laminating Ti and Al.

[0170]

Hereat, the n-electrode 211a is an ohmic electrode which was brought in ohmic contact with the exposed face 203a of the n-type layer 203. After forming the p-side electrode 210 and the n-side electrode 211a for ohmic, the respective electrodes are brought in ohmic contact by being annealed by heat treatment. The p-side ohmic electrode which was obtained at this time becomes an opaque film which hardly transmit the luminescence of the active layer 204.

[0171]

Successively, an insulation film comprising SiO_2 is formed on the portion or the whole surface excluding the whole of the above-mentioned p-side electrode 210 and the n-side electrode 211a, namely, the insulation film comprising SiO_2 is formed on the whole element surfaces such as the exposed face 203a of the n-type layer 203 and the side face of said exposed face 203a. After formation of the insulation film, the pat electrodes for bonding are respectively formed on the surfaces of the p-side electrode 210 and the n-side electrode 211a which were exposed from the insulation film, and electrically conducted with the respective electrodes for ohmic. The p-side pat electrode 210b and the n-side pat electrode 211b are respectively formed by laminating Ni, Ti and Au on the respective electrodes for ohmic.

[0172]

Finally, the light-emitting elements having a length of 300 μm at one side are obtained by dividing the substrate 201.

[0173]

The luminescence peak wavelength is about 400nm.

[0174]

BaSi₂O₂N₂:Eu of Example 1, (Ca_{0.93}, Eu_{0.05}, Mn_{0.02})₁₀(PO₄)₆Cl₂, (Y, Gd)₃(Al, Ga)₅O₁₂:Ce and SrCaSi₅N₈:Eu are used for the light-emitting devices of Examples 1, but the compounding ratio can be appropriately varied. These phosphors are irradiated using the excitation light source of Ex = 400nm. These phosphors absorb light from the excitation light source, carry out wavelength conversion, and have a fixed luminescence wavelength. BaSi₂O₂N₂:Eu of Example 83 has the luminescence peak wavelength at 470nm to 530nm. (Ca_{0.93}, Eu_{0.05}, Mn_{0.02})₁₀(PO₄)₆Cl₂ has the luminescence peak wavelength at 440 to 500nm. (Y, Gd)₃(Al, Ga)₅O₁₂:Ce has the luminescence peak wavelength at 500 to 650nm. SrCaSi₅N₈:Eu has the luminescence peak wavelength at 580nm to 730nm.

[0175]

(Properties of the light-emitting device of Example 1)

Table 3 shows the properties and color rendering of the light-emitting device of Example 1. However, the properties and color rendering of the light-emitting device of Example 1 are simulation, and when the light-emitting device is practically produced, it is considered that self absorption occurs and the deviation of wavelength is generated. As the light-emitting device of Comparative Example 1, the excitation light source of Ex = 400nm is used and (Ca_{0.93}, Eu_{0.05}, Mn_{0.02})₁₀(PO₄)₆Cl₂ and (Y, Gd)₃(Al, Ga)₅O₁₂:Ce are used.

[0176]

Table 3

	Luminescence properties (Ex=400nm)			
	Color tone x	Color tone y	Color temperature (K)	Visual sensitivity efficiency (%)
Light emitting device of Comparative Example 1	0.356	0.371	4693	100
Light emitting device of Example 1	0.363	0.365	4449	81.5

	Average color rendering index	Specific color rendering index						
	Ra	R1	R2	R3	R4	R5	R6	R7
Light emitting device of Comparative Example 1	76.0	74.7	90.9	92.8	60.2	69.9	82.0	78.9
Light emitting device of Example 1	88.2	94.6	89.3	84.6	85.9	92.0	86.2	84.8

	Specific color rendering index							
	R8	R9	R10	R11	R12	R13	R14	R15
Light emitting device of Comparative Example 1	58.3	-1.9	71.8	52.2	41.9	79.8	96.4	70.1
Light emitting device of Example 1	88.1	96.1	75.7	89.9	75.3	92.4	91.3	92.4

The phosphors excited by the light-emitting element at 400nm excitation have respectively the luminescence peak wavelengths at a blue green to green region in case of $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 83, at a blue purple to blue region in case of $(\text{Ca}_{0.93}, \text{Eu}_{0.05}, \text{Mn}_{0.02})_{10}(\text{PO}_4)_6\text{Cl}_2$, at a green to yellow red region in case of $(\text{Y}, \text{Gd})_3(\text{Al}, \text{Ga})_5\text{O}_{12}\text{:Ce}$ and at a yellow red to red region in case of $\text{SrCaSi}_5\text{N}_8\text{:Eu}$. It exhibits a luminescence color at a white region by the color mixture of lights from these phosphors. The light-emitting device of Example 88 exhibits a luminescence color at a white region. Further, since the excitation light source nearby 400nm having low visual sensitivity property is used, the color tone can be easily changed by changing the compounding ratio of the phosphors. In particular, the average color rendering index (Ra) was 76.0 for a white light-emitting device which was shown in Comparative Example 1, but the average color rendering index (Ra) was 88.1 for the white light-emitting device related to Example 88, which was extremely good. Color rendering is improved thereby. Further, the color rendering is improved at almost all of color chips with respect to the specific color rendering index (R1 to R15). Furthermore, the specific color rendering index (R9) is -1.9 for a white light-emitting device which was shown in Comparative Example 1, but the specific color rendering index (R9) is 96.1 for the white light-emitting device related to Example 88,

which was extremely good. The specific color rendering index (R9) is a red color chip having comparatively high chroma. Visual sensitivity efficiency is represented by a relative value when the white light-emitting device of Comparative Example 1 was 100%. [0177]

The light-emitting devices of Examples 2 and 3 relate to a white light-emitting device using a light-emitting element having a luminescence spectrum of 460 nm the excitation light source. Fig. 1 is a diagram showing the light emitting device of the present invention. Fig. 13 is a chart showing the luminescence spectra (simulation) of the light-emitting devices of Examples 2 and 3.

[0178]

(light-emitting element)

In the light-emitting devices of Examples 2 and 3, the semiconductor layer 2 of an n-type GaN layer and p-type GaN layer is formed on the sapphire substrate 1, the electrode 3 is provided at said n-type and p-type semiconductor layers 2, said electrode 3 is electrically connected with the lead frame 13 by the electroconductive wire 14. The upper portion of the light-emitting device 10 is covered with the phosphor 11 and the coating member 12, and the outer peripheral portions of the lead frame 13, the phosphor 11 and the coating member 12 are covered with the mold member 15. The semiconductor layer 2 is obtained by laminating n⁺GaN:Si, n-AlGaInN:Si, n-GaN, GaInN QWs, p-GaN:Mg, p-AlGaInN:Mg, and p-GaN:Mg in order on the sapphire substrate 1. The portion of said n⁺GaN:Si is etched and an n-type electrode is formed. A p-type electrode is formed on said p-GaN:Mg layer. Copper with Fe is used for the lead frame 13. A cup for mounting the light-emitting device 10 is provided on the upper portion of the mount lead 13a, and the light-emitting element 10 is die-bonded at about the central part bottom of said cup. Gold is used for the electroconductive wire 14, and Ni plating is carried out on the bump 4 for electrically connecting the electrode 3 with the electroconductive wire 14. As the coating member 12, a mixture which mixed an epoxy resin and a dispersant, barium titanate, titanium oxide and the fore-mentioned phosphor 11 at a fixed proportion is used. The epoxy

resin is used for the mold member 15. The cannonball type light-emitting device 1 is a column in which the mold member 15 is a radius of 2 to 4mm, height is about 7 to 10mm, and the upper part is a hemisphere.

[0179]

When current is run in the light-emitting devices of Examples 2 and 3, the blue light-emitting element 10 having the luminescence spectrum with a peak wave length of about 460nm emits light. The phosphor 11 which covers the semiconductor layer 2 carries out the conversion of color tone. As a result, there can be provided the light-emitting device of Example 29 which emits white light.

[0180]

(Phosphors)

The phosphor 11 used in the light-emitting devices of Example 2 and 3 related to the present invention is a phosphor mixing the oxynitride phosphor of Example 1, a YAG phosphor represented by $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$, and a nitride phosphor represented by $CaSrSi_5N_8:Eu$. Said phosphor 11 is mixed together with the coating member 12. The compounding ratio can be varied. These phosphors are irradiated using the excitation light source of $\lambda = 460nm$. These phosphors 11 absorb light from said excitation light source, carry out the wavelength conversion, and have a fixed luminescence wavelength. The $BaSi_2O_2N_2:Eu$ of Example 1 has the luminescence peak wavelength at 470nm to 530nm. $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$ has the luminescence peak wavelength at 500 to 650nm. $SrCaSi_5N_8:Eu$ has the luminescence peak wavelength at 580nm to 730nm.

[0181]

In the light-emitting devices of Examples 2 and 3, the portion of the light of the light-emitting element 10 transmits. Further, the portion of the light of the light-emitting element 10 excites the phosphor 11, carries out the wavelength conversion, and said phosphor 11 have a fixed luminescence wavelength. There can be provided the light-emitting device which emits white light, by the color mixture of the blue light from these light-emitting element 10 and the light from the phosphor 11.

[0182]

(Properties of light-emitting devices of Examples 2 and 3)

Table 4 shows the properties and color rendering of the light-emitting devices of Examples 2 and 3. However, the properties and color rendering of the light-emitting devices of Examples 2 and 3 are simulation, and when the light-emitting device is practically produced, it is considered that self absorption occurs and the deviation of wavelength is generated. As the light-emitting device of Comparative Example 2, the excitation light source of $\text{Ex} = 460\text{nm}$ is used and $(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}:\text{Ce}$ is used. Further, Examples 2 and 3 are the luminescence spectrum when the peak values are the same.

[0183]

Table 4

	Luminescence properties ($\text{Ex}=460\text{nm}$)			
	Color tone x	Color tone y	Color temperature (K)	Visual sensitivity efficiency (%)
Light emitting device of Comparative Example 2	0.356	0.371	4693	100
Light emitting device of Example 2	0.352	0.358	4773	86.1
Light emitting device of Example 3	0.356	0.360	4643	81.8

	Average color rendering index	Specific color rendering index						
	Ra	R1	R2	R3	R4	R5	R6	R7
Light emitting device of Comparative Example 2	76.0	74.7	90.9	92.8	60.2	69.9	82.0	78.9
Light emitting device of Example 2	84.5	93.9	92.3	85.2	72.4	86.5	91.3	77.5
Light emitting device of Example 3	83.1	93.5	86.0	79.9	96.0	88.0	83.2	96.6

	Specific color rendering index							
	R8	R9	R10	R11	R12	R13	R14	R15
Light emitting device of Comparative Example 2	58.3	-1.9	71.8	52.2	41.9	79.8	96.4	70.1
Light emitting device of Example 2	77.1	70.7	87.0	73.8	63.1	97.9	92.4	88.0
Light emitting device of Example 3	81.5	94.1	70.5	81.3	65.0	90.8	89.2	88.3

The luminescence spectra of the phosphors excited by light of 460nm from the light-emitting element have respectively the luminescence peak wavelengths at a blue green to green region in case of $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 83, at a green to yellow red region in case of $(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}\text{:Ce}$ and at a yellow red to red region in case of $\text{SrCaSi}_5\text{N}_8\text{:Eu}$. It exhibits a luminescence color at a white region by the color mixture of lights from these phosphors. The light-emitting devices of Examples 89 and 90 exhibit a luminescence color at a white region as a whole. Further, since visual light nearby 460nm as the excitation light source is used and the phosphor emitting blue light is not used, there is little loss of luminescence efficiency in accordance with the wavelength conversion. Further, the color tone can be easily changed by changing the compounding ratio of the phosphors. In particular, the average color rendering index (Ra) was 76.0 for a white light-emitting device which was shown in Comparative Example 2, but the average color rendering indices (Ra) were 84.5 and 83.1 for the white light-emitting devices related to Examples 2 and 3, which was extremely good. Color rendering is improved thereby. Further, the color rendering is improved at almost all of color chips with respect to the specific color rendering index (R1 to R15). Furthermore, the specific color rendering index (R9) is -1.9 for a white light-emitting device which was shown in Comparative Example 2, but the specific color rendering indices (R9) are 70.7 and 94.1 for the white light-emitting devices related to Examples 2 and 3, which were extremely good. The specific color rendering indices (R9) are a red color chip having comparatively high chroma. Visual

sensitivity efficiency is represented by a relative value when the white light-emitting device of Comparative Example was 100%.

[0184]

<Light-emitting device>

The light-emitting device of Example 4 relates to a white light-emitting device using a light-emitting element having the luminescence peak wavelength at 457nm, as an excitation light source. The basic structure is the structure shown in Fig. 1. Fig. 14 is a chart showing the luminescence spectra of the light-emitting devices of Examples 4 and 5.

[0184]

(Light-emitting element)

When current is run in the light-emitting device of Example 4, the blue light-emitting element 10 having a peak wave length at about 457nm emits light. The phosphor 11 which covers the semiconductor layer 2 carries out the conversion of color tone. As a result, there can be provided the light-emitting device of Example 4 which emits white light.

[0186]

(Phosphor)

The phosphor 11 used for the light-emitting device of Example 4 related to the present invention uses the phosphors 11 which mixed the oxynitride phosphor of Example 1, the YAG phosphor represented by $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$ and the nitride phosphor represented by $SrCaSi_5N_8:Eu$. Said phosphor 11 is mixed with the coating member 12. The compounding ratio can be appropriately changed. These phosphors 11 are irradiated using the excitation light source of $\lambda = 457nm$. These phosphors 11 absorb light from said excitation light source, carry out the wavelength conversion, and have a fixed wavelength. $BaSi_2O_2N_2:Eu$ of Example 83 has the luminescence peak wavelength at 470nm to 530nm. $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$ has the luminescence peak wavelength at 500 to 650nm. $SrCaSi_5N_8:Eu$ has the luminescence peak wavelength at 580nm to 730 nm.

[0187]

The portion of light of the light-emitting element 10 transmits the light-emitting device of Example 4. Further, the portion of the light of the light-emitting element 10 excites the phosphors 11 and carries out the wavelength conversion, and said phosphors 11 have a fixed luminescence wavelength. There can be provided the light-emitting device which emits white light, by the color mixture of the blue light from these light-emitting elements 10 and the light from the phosphors 11.

[0188]

(Properties of light-emitting device of Example 4)

Table 5 shows the properties and color rendering of the light-emitting device of Example 4.

[0189]

Table 5

	Luminescence properties (Ex=457nm)								
	Current If(mA)	Voltage Vf(V)	Radiation analysis (mW)	Brightness (beam) (lm)	Luminescence peak wavelength (nm)	Color tone x	Color tone y	Color temperature (K)	Lamp efficiency (lm/W)
Light emitting device of Example 4	20	3.38	6.3	1.69	453	0.334	0.340	5443	25.0

	Average color rendering index	Specific color rendering index						
	Ra	R1	R2	R3	R4	R5	R6	R7
Light emitting device of Example 4	92.7	96.6	94.8	90.5	93.8	95.7	91.6	89.8

	Specific color rendering index						
	R8	R9	R10	R11	R12	R13	R14
Light emitting device of Example 4	89.0	83.0	88.7	96.4	81.0	96.8	94.4

The phosphors excited by the light-emitting element of 457nm excitation have respectively the luminescence peak wavelengths at a blue green to green region in case of $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 1, at a green to yellow red region in case of $(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}\text{:Ce}$ and at a yellow red to red region in case of $\text{SrCaSi}_5\text{N}_8\text{:Eu}$. The light-emitting device of Example 4 exhibits a luminescence color at a white region by the color mixture of lights from these phosphors. Further, since visual light nearby 457nm as the excitation light source is used and the phosphor emitting blue light is not used, there is little loss of luminescence efficiency accompanied with the wavelength conversion. Further, the color tone can be easily changed by changing the compounding ratio of the phosphors. The white light-emitting device of Example 4 exhibits extremely high luminescence efficiency in which lamp efficiency is 25.0lm/W. The average color rendering index(Ra) was 92.7 for the white light-emitting device related to Example 91, which was extremely good. Color rendering is improved thereby. Further, the color rendering is improved at almost all of color chips with respect to the specific color rendering index (R1 to R15). Furthermore, the specific color rendering index (R9) is 83.0 for the white light-emitting device related to Example 4, which was extremely good.

[0190]

Therefore, the white light-emitting device of Example 4 can provide a light-emitting device with superior color rendering.

[0191]

< light-emitting device >

The light-emitting device of Example 5 relates to a white light-emitting device using a light-emitting element having the luminescence peak wavelength at 463nm, as an excitation light source. The basic structure is the structure shown in Fig. 1. Fig. 14 is a chart showing the luminescence spectra of the light-emitting devices of Examples 4 and 5.

[0192]

(Light-emitting element)

When current is run in the light-emitting device of Example 5, the blue

light-emitting element 10 having a peak wave length at about 463nm emits light. The phosphor 11 which covers the semiconductor layer 2 converts the color tone of the blue light. As a result, there can be provided the light-emitting device of Example 5 which emits white light.

[0193]

(Phosphor)

The phosphor 11 used for the light-emitting device of Example 5 uses the phosphors 11 which mixed the oxynitride phosphor of Example 1, the YAG phosphor represented by $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$ and the nitride phosphor represented by $CaSrSi_5N_8:Eu$. Said phosphors 11 are mixed with the coating member 12. The compounding ratio can be appropriately changed. These phosphors 11 are irradiated using the excitation light source of $\lambda = 463nm$. These phosphors 11 absorb light from said excitation light source, carry out the wavelength conversion, and have a fixed wavelength. $BaSi_2O_2N_2:Eu$ of Example 1 has the luminescence peak wavelength at 470nm to 530nm. $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$ has the luminescence peak wavelength at 500nm to 650nm. $SrCaSi_5N_8:Eu$ has the luminescence peak wavelength at 580 to 730nm.

[0194]

The portion of light of the light-emitting element 10 transmits the light-emitting device of Example 5. Further, the portion of the light of the light-emitting element 10 excites the phosphors 11 and carries out the wavelength conversion, and said phosphors 11 have a fixed luminescence wavelength. There can be provided the light-emitting device which emits white light, by the color mixture of the blue light from these light-emitting elements 10 and the light from the phosphors 11.

[0195]

(Properties of light-emitting device of Example 5)

Table 6 shows the properties and color rendering of the light-emitting device of Example 5.

Table 6

	Luminescence properties (Ex=463nm)								
	Current If(mA)	Voltage Vf(V)	Radiation analysis (mW)	Brightness (beam) (lm)	Luminescence peak wavelength (nm)	Color tone x	Color tone y	Color temperature (K)	Lamp efficiency (lm/W)
Light emitting device of Example 5	20	3.28	5.4	1.397	460	0.327	0.334	5751	21.3

	Average color rendering index	Specific color rendering index						
	Ra	R1	R2	R3	R4	R5	R6	R7
Light emitting device of Example 5	84.9	90.9	86.3	81.6	83.2	88.1	82.2	81.4

	Specific color rendering index						
	R8	R9	R10	R11	R12	R13	R14
Light emitting device of Example 5	85.8	91.0	69.9	88.0	70.7	88.9	89.6

The phosphors excited by the light-emitting element of 463nm excitation have respectively the luminescence peak wavelengths at a blue green to green region in case of $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 1, at a green to yellow red region in case of $(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}\text{:Ce}$ and at a yellow red to red region in case of $\text{SrCaSi}_5\text{N}_8\text{:Eu}$. The light-emitting device of Example 5 exhibits a luminescence color at a white region by the color mixture of lights from these phosphors. Thus, the light-emitting device of Example 5 exhibits a luminescence color at a white region. Further, since visual light nearby 463nm as the excitation light source is used and the phosphor emitting blue light is not used, there is little loss of luminescence efficiency accompanied with the wavelength conversion. Further, the color tone can be easily changed by changing the compounding ratio of the phosphors. The white light-emitting device of Example 5 exhibits extremely high

luminescence properties in which lamp efficiency is 21.3lm/W. The average color rendering index(Ra) was 84.9 for the white light-emitting device related to Example 5, which was extremely good. Color rendering is improved thereby. Further, the color rendering is improved at almost all of color chips with respect to the specific color rendering index (R1 to R15). Furthermore, the specific color rendering index (R9) is 91.0 for the white color light-emitting device related to Example 5, which was extremely good.

[0197]

The white color light-emitting device of Example 4 can provide a light-emitting device with superior color rendering, thereby.

[0198]

<Light-emitting device>

Fig. 15 is a chart showing the cap type light-emitting device of Example 6.

[0199]

In Example 6, the same codes are imparted for the same members as those in the light-emitting device of Example 1 and illustrations thereof are abbreviated. As the light-emitting element 10, a light-emitting element having the luminescence peak wavelength at 400nm is used.

[0200]

The light-emitting device of Example 6 is constituted by covering the cap 16 comprising a transparent resin in which phosphors (not illustrated) were dispersed on the surface of the mold member of the light-emitting device of Example 1.

[0201]

A cup for mounting the light-emitting device 10 is provided on the upper portion of the mount lead 13a, and said light-emitting element 10 is die-bonded at about the central part bottom of said cup. The phosphor 11 is provided on the upper part of said cap so as to cover the light-emitting element 10 in the light-emitting device of Example 6, but the phosphor may be contained only in the cap in the light-emitting device of Example 1. When the phosphor 11 is not provided on the light-emitting element 10, the phosphor is

able not to directly receive the influence of heat generated from the light-emitting element 10.

[0202]

Further, the phosphor is homogeneously dispersed in a transparent resin in case of the cap 16. The transparent resin containing the phosphor is molded in a shape which is fitted for the shape of the mold member 15. Alternatively, there is also possible a process of charging the transparent resin containing the phosphor into a fixed mold, then pushing the light-emitting device 1 into said mold and molding it. As the specific example of the transparent resin of the cap 16, there are used transparent resins excellent in temperature properties and weather resistance such as an epoxy resin, a urea resin and a silicone resin; silica sol, glass, an inorganic binder and the like. In addition to the resins mentioned above, there can be also used thermosetting resins such as a melamine resin and a phenol resin. Further, there can be also used thermoplastic resins such as a polyethylene, a polypropylene, a poly(vinyl chloride) and a polystyrene; thermoplastic rubbers such as a styrene-butadiene block copolymer and a segmented polyurethane, etc. Further, a dispersant, barium titanate, titanium oxide, aluminum oxide and the like may be contained together with the phosphor. Further, a light stabilizer and a coloring agent may be contained. The nitride phosphor of $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu}$ and the phosphor of $(\text{Ca}_{0.95}\text{Eu}_{0.05})_{10}(\text{PO}_4)_6\text{Cl}_2$ are used for the phosphors contained in the cap 16. The nitride phosphor of Example 3 is used for the phosphor 11 used in the cap of the mount lead 13a. However, since the phosphors are used in the cap 16, there may be a structure in which the cap 16 contains the oxynitride phosphor and only the coating member 12 exists in the cap of the mount lead 13a.

[0203]

In the light-emitting device thus constituted, the portion of light emitted from the light-emitting element 10 excites the oxynitride phosphor of the phosphor 11 and green light is emitted from the oxynitride phosphor. Further, the portion of light emitted from the light-emitting element 10 or the portion of light emitted from the oxynitride phosphor

excites the phosphor of the cap 16, and red light is emitted from blue and yellow. The green light of the oxynitride phosphor is mixed with the red light from the blue color and yellow color of the phosphor of the cap 16, and as a result, white light is released from the surface of the cap 16.

[0204]

[EFFECT OF THE INVENTION]

Accordingly, the present invention relate to oxynitride phosphors which absorb a light by an excitation light source at an ultraviolet to visible light region and which has a luminescence color different from the luminescence color of the excitation light source. The oxynitride phosphors have a peak wavelength in a range from blue green to green region and extremely light luminescent efficiency. The oxynitride phosphors are superior in temperature characteristic. When the activator R = 1 : 0.005 to 1 : 0.15 based on the fore-mentioned Group II element, the luminescent efficiency is maximum.

[0205]

According to the present invention, a process of producing the oxynitride phosphors with easily and good re-productivity can be provided.

[0206]

The present invention relates to the light emitting device which has the oxynitride phosphor and light emitting element. The light emitting device emits a bright light in a range from blue to green. The light emitting which have a combination of the oxynitride phosphor and the second phosphor of blue, green and red can be produced. With this, the light emitting device which can emit a white light and which is superior in rendering property can be produced. The light emitting which have a combination of the oxynitride phosphor, the second phosphor of YAG phosphor and a blue light emitting element can be produced. With this, the light emitting device which can emit a white light and which has high luminescent efficiency and good rendering property can be provided. In the rendering property, red rendering property is improved. Therefore, the present invention has excellent technical meanings that the fore-mentioned light emitting device can be

provided.

[BRIEF DESCRIPTION OF DRAWING]

Fig. 1 is a view showing the cannonball type light-emitting device related to the present invention;

Fig. 2(a) is a plane view showing the surface mounting type light-emitting device related to the present invention, and Fig. 2(b) is a section view showing the surface mounting type light-emitting device related to the present invention;

Fig. 3 is a process chart showing the production process of the oxynitride phosphors of Example 1 to 5;

Fig. 4 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $\text{Ex} = 400\text{nm}$;

Fig. 5 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $\text{Ex} = 460\text{nm}$;

Fig. 6 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 7 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 8 is an SEM photo photographing the oxynitride phosphor of Example 1;

Fig. 9 is a plane view showing the light-emitting element related to the present invention;

Fig. 10 is a section view showing the A-A' of the light-emitting element related to the present invention;

Fig. 11 is a chart showing the cap type light-emitting device of Example 1 related to the present invention;

Fig. 12 is a chart showing the luminescence spectrum (simulation) of the light-emitting devices of Examples 1 to 3;

Fig. 13 is a chart showing the chromaticity coordinates (simulation) of the light-emitting devices of Examples 2 to 3;

Fig. 14 is a chart showing the luminescence spectra (simulation) of the light-emitting devices of Examples 4 and 5; and

Fig. 15 is a chart showing the luminescence spectra of the light-emitting device of Example 6.

[EXPLANATIONS OF NUMERALS]

- 1: substrate
- 2: semiconductor layer
- 3: electrode
- 4: bump
- 10: light emitting element
- 11: phosphor
- 12: coating member
- 13: lead frame
- 13a: mount lead
- 13b: inner lead
- 14: electro-conductive wire
- 15: mold member
- 101: light emitting element
- 102: lead electrode
- 103: insulation seal member
- 104: electro-conductive wire
- 105: package
- 106: rid
- 107: window portion
- 108: phosphor
- 109: Coating member
- 201: Substrate
- 202: groundwork layer

203: n-type layer

203a: exposed plane

204: active layer

205: p-side carrier confining layer

206: first p-layer

207: current diffusion layer

208: p-side contact layer

209: light emission portion

210: p-side electrode

210a: electrode branch

210b: p-side pat electrode

211a: n-side electrode

211b: n-side pat electrode

Fig. 1

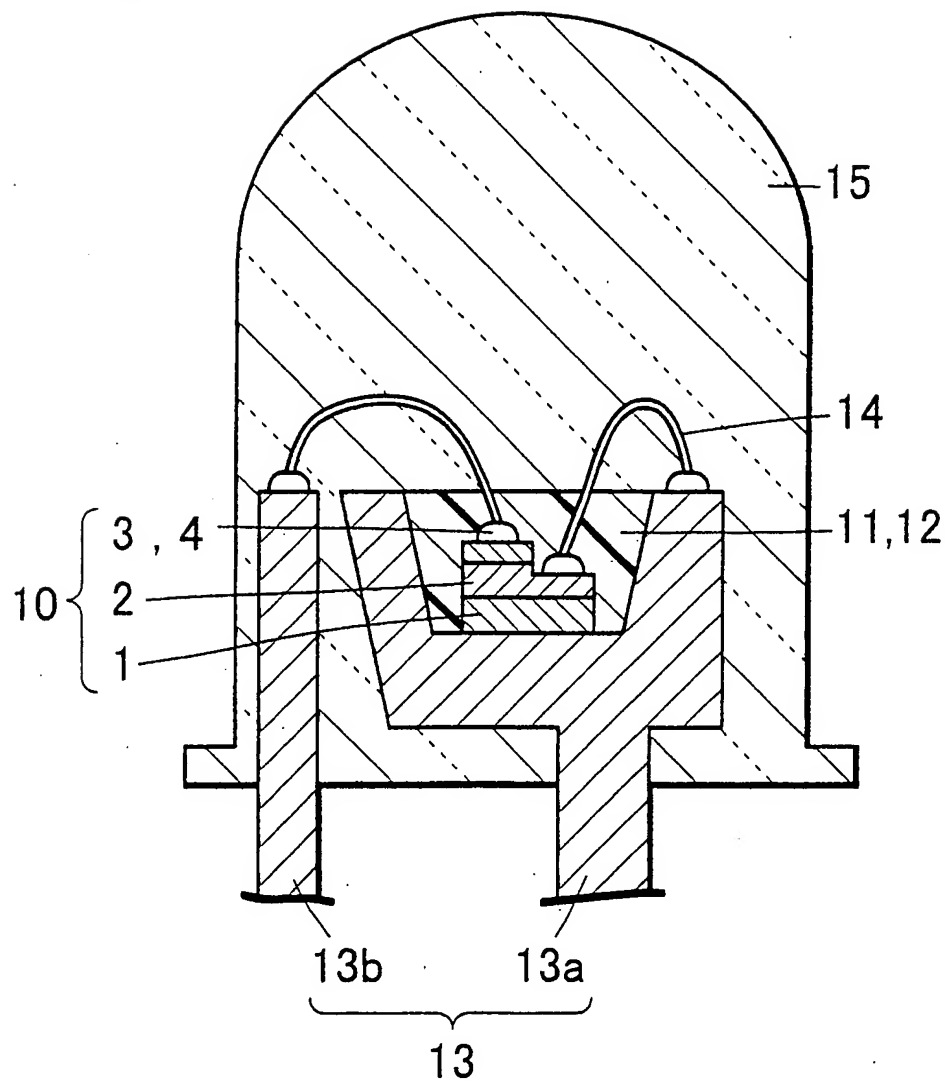
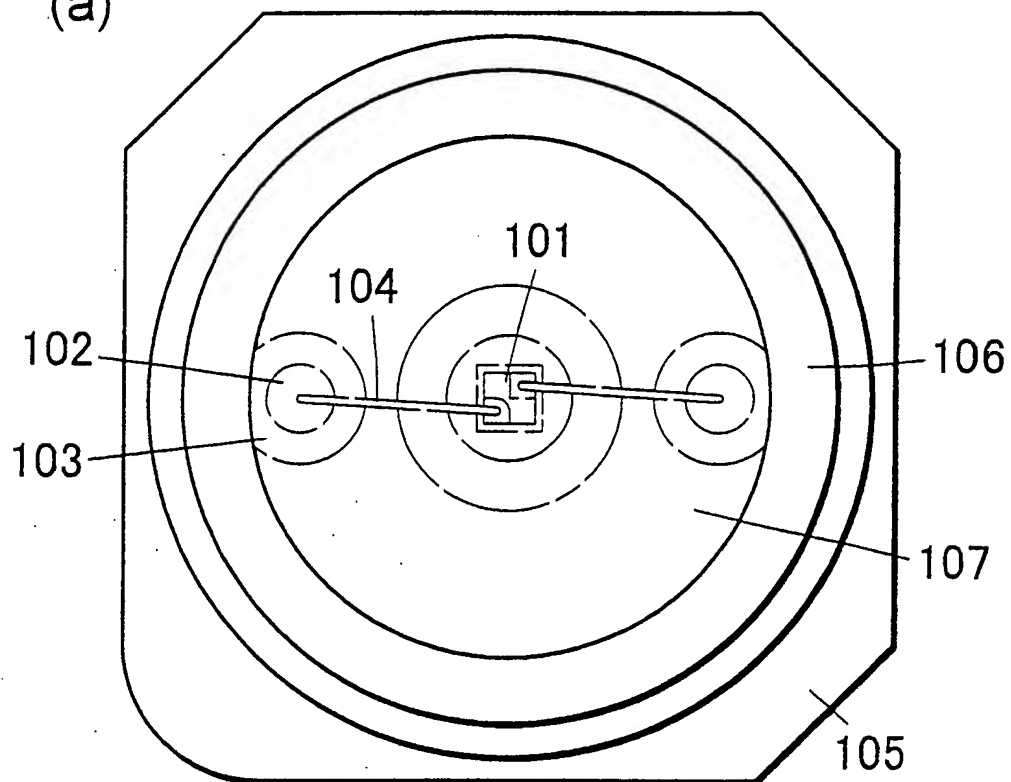


Fig. 2

(a)



(b)

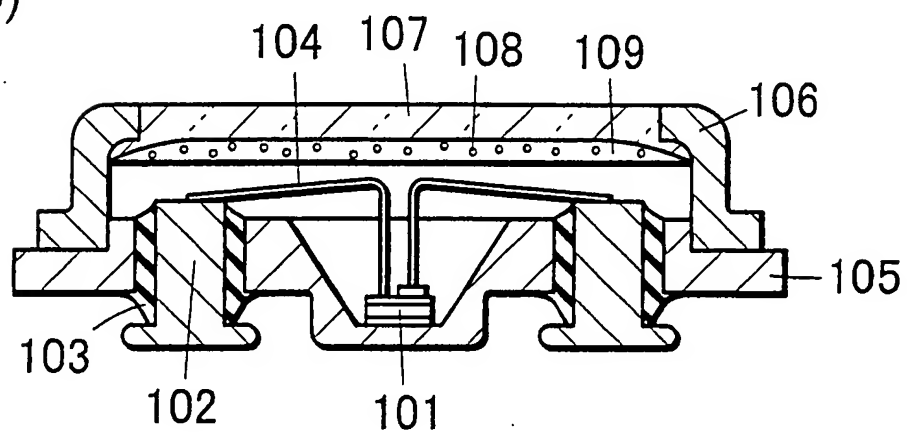


Fig. 3

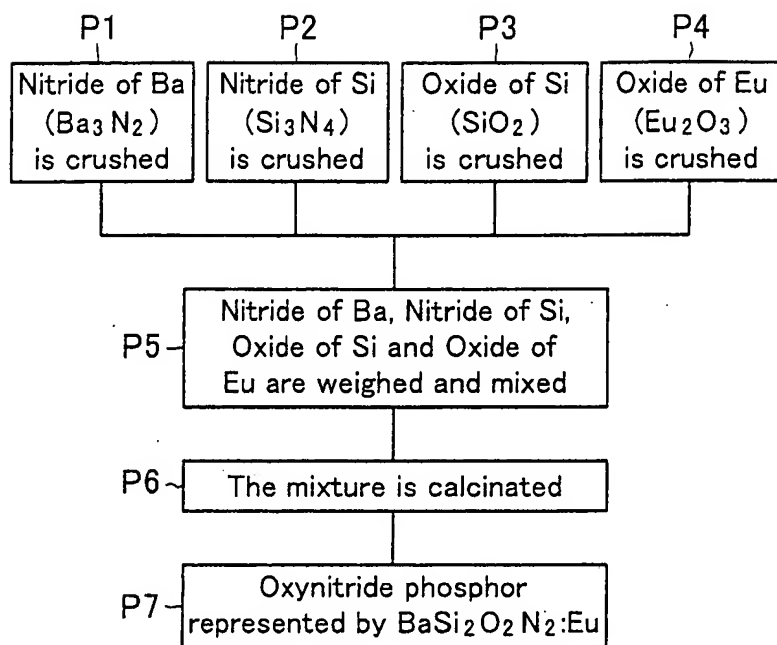


Fig. 4

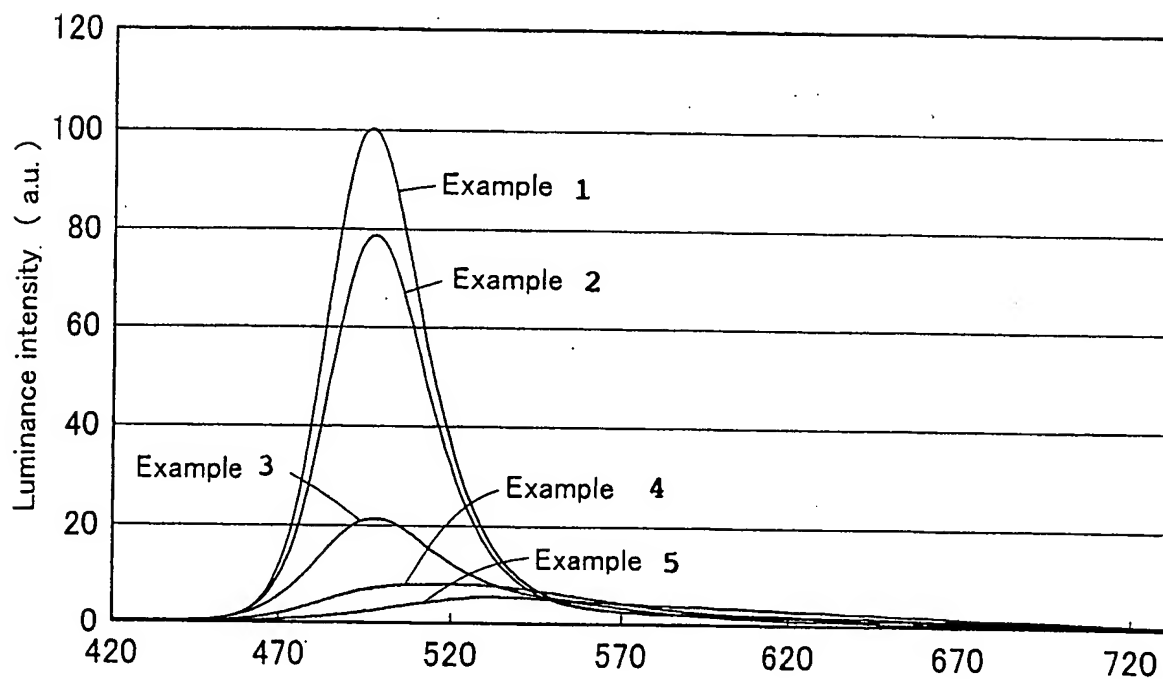


Fig. 5

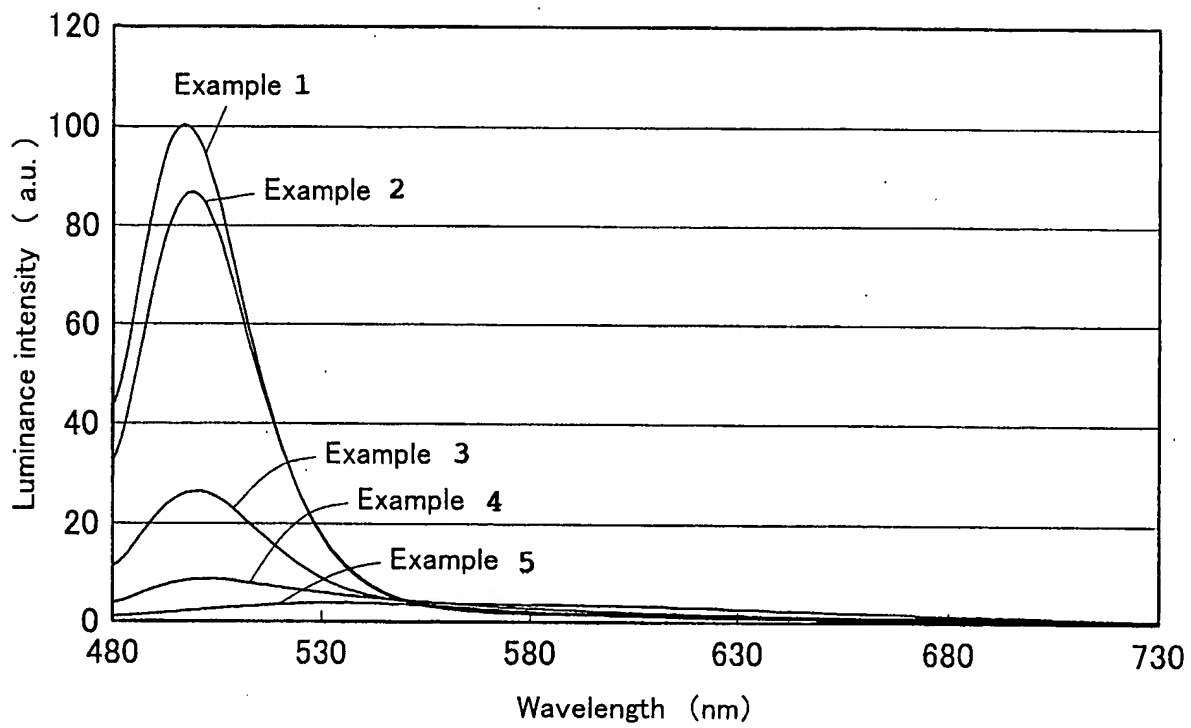


Fig. 6

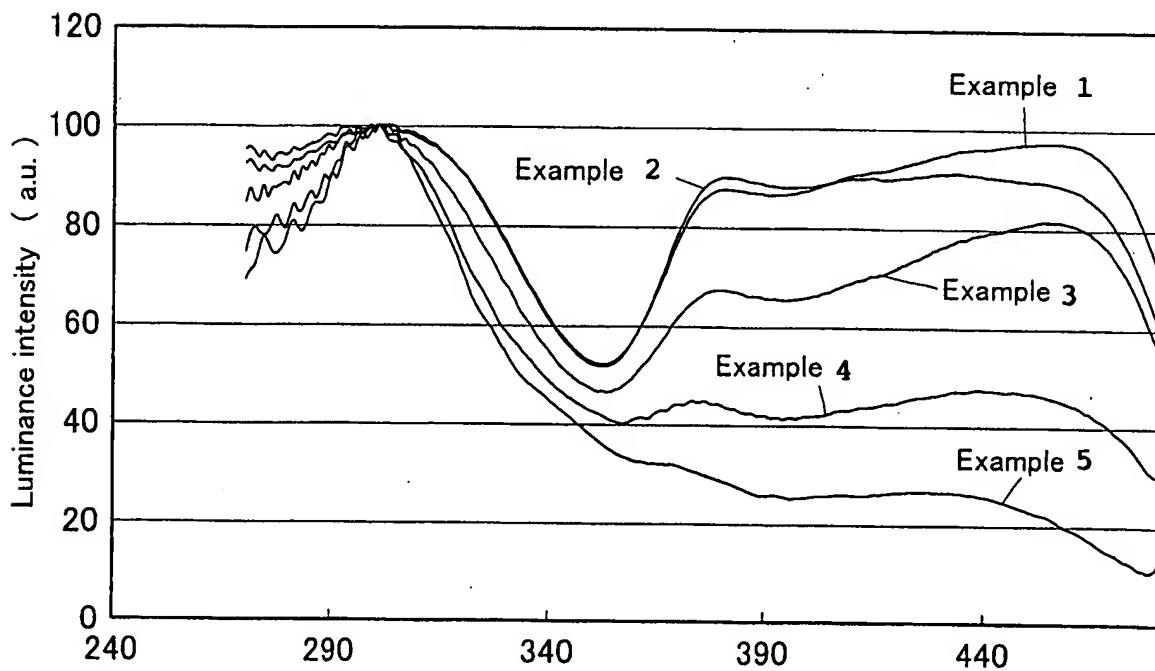


Fig. 7

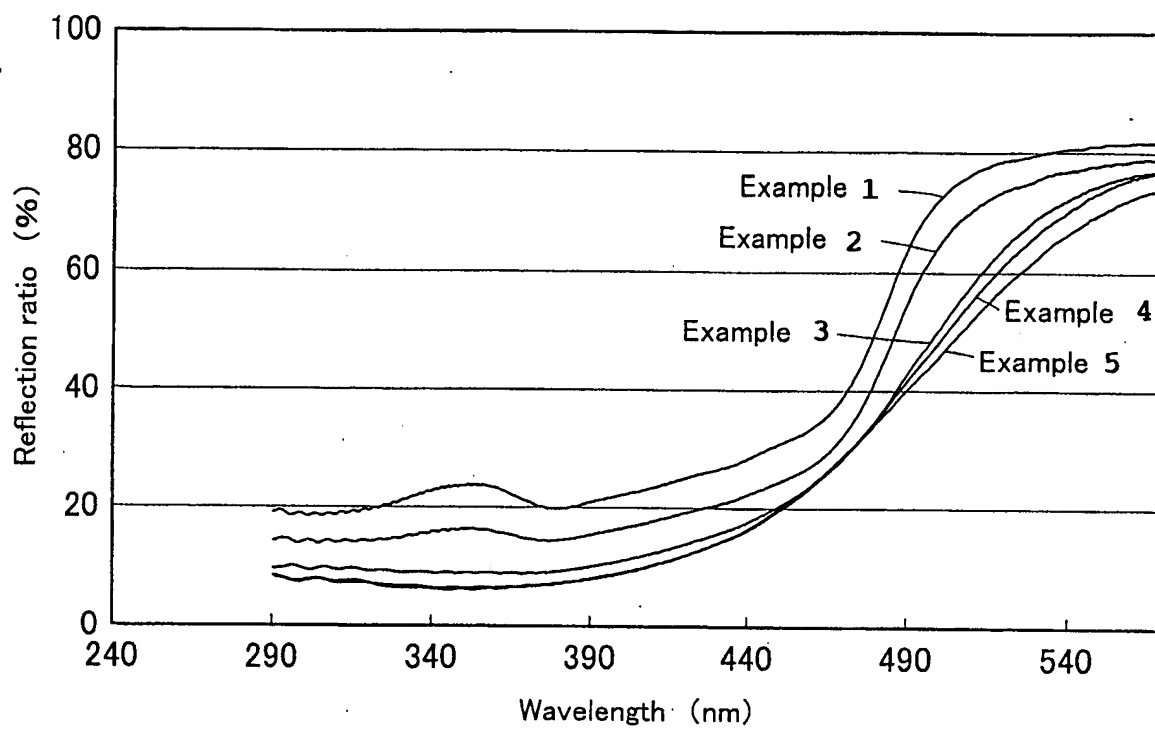
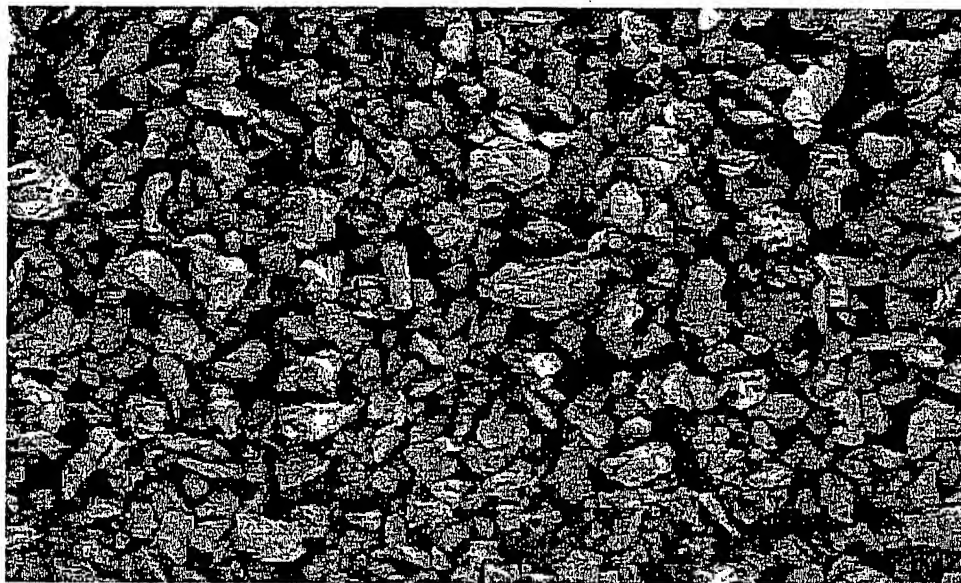


Fig. 8

(a)



(b)

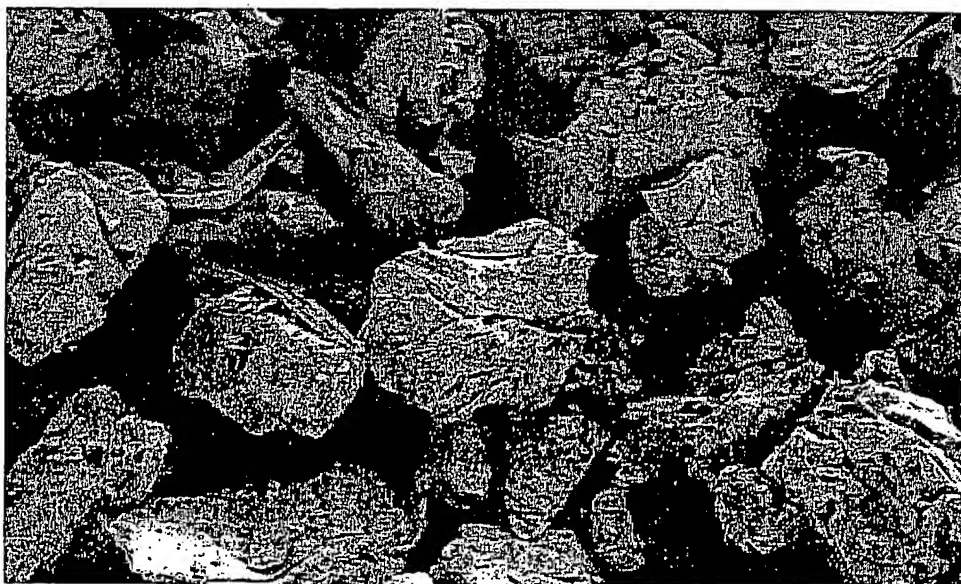


Fig. 9

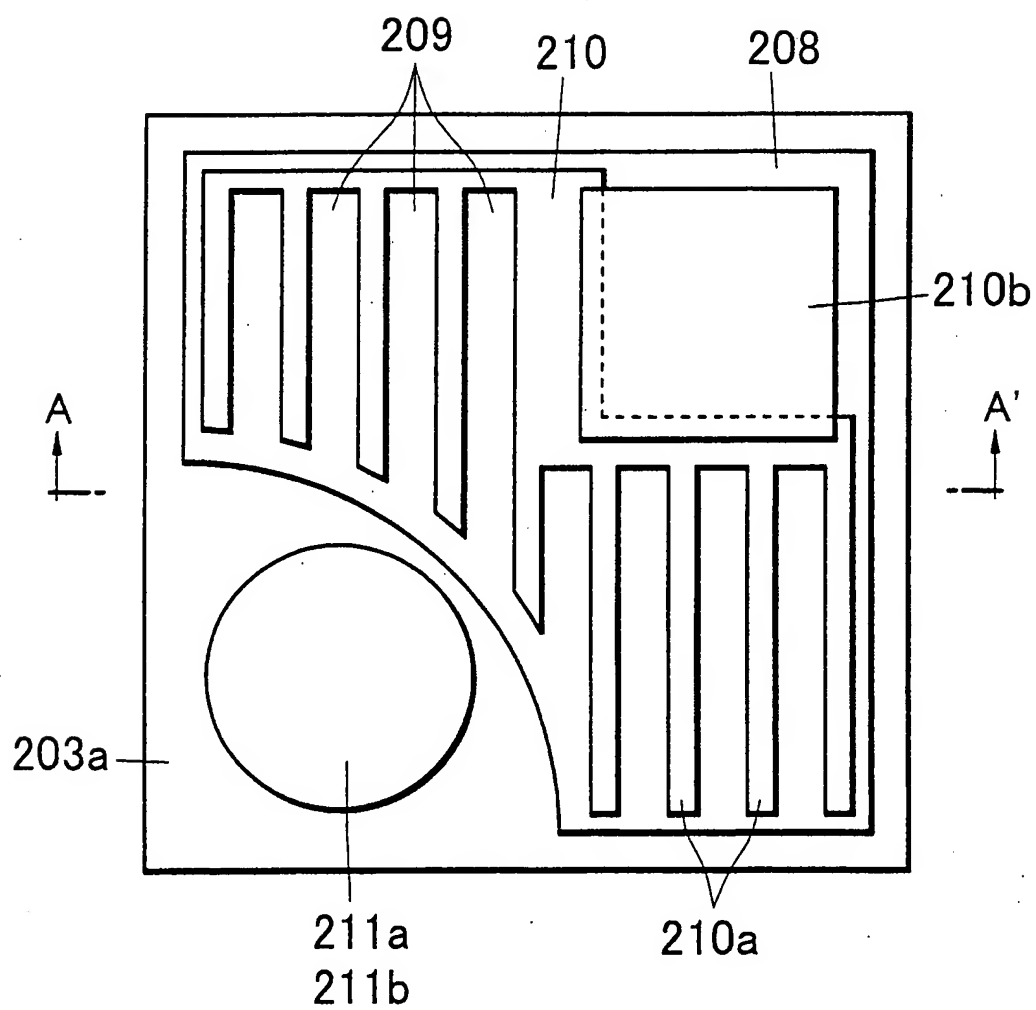


Fig. 10

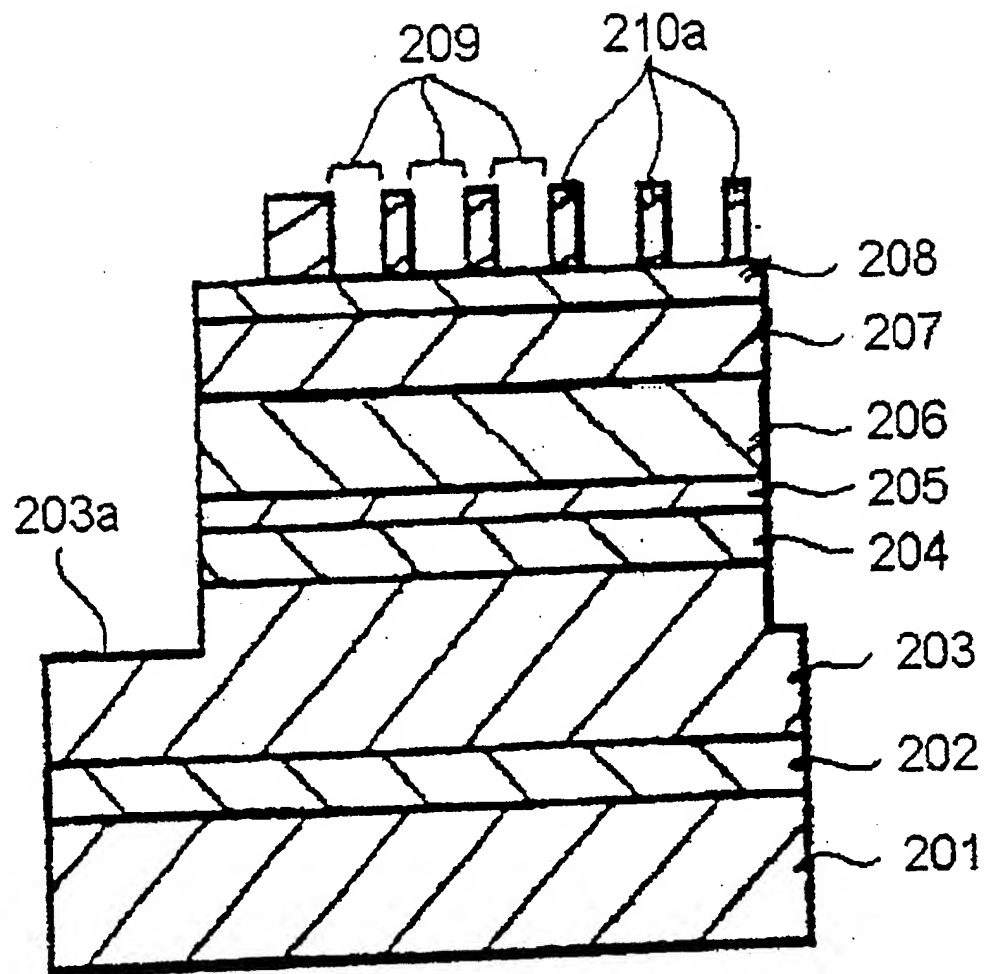


Fig. 11

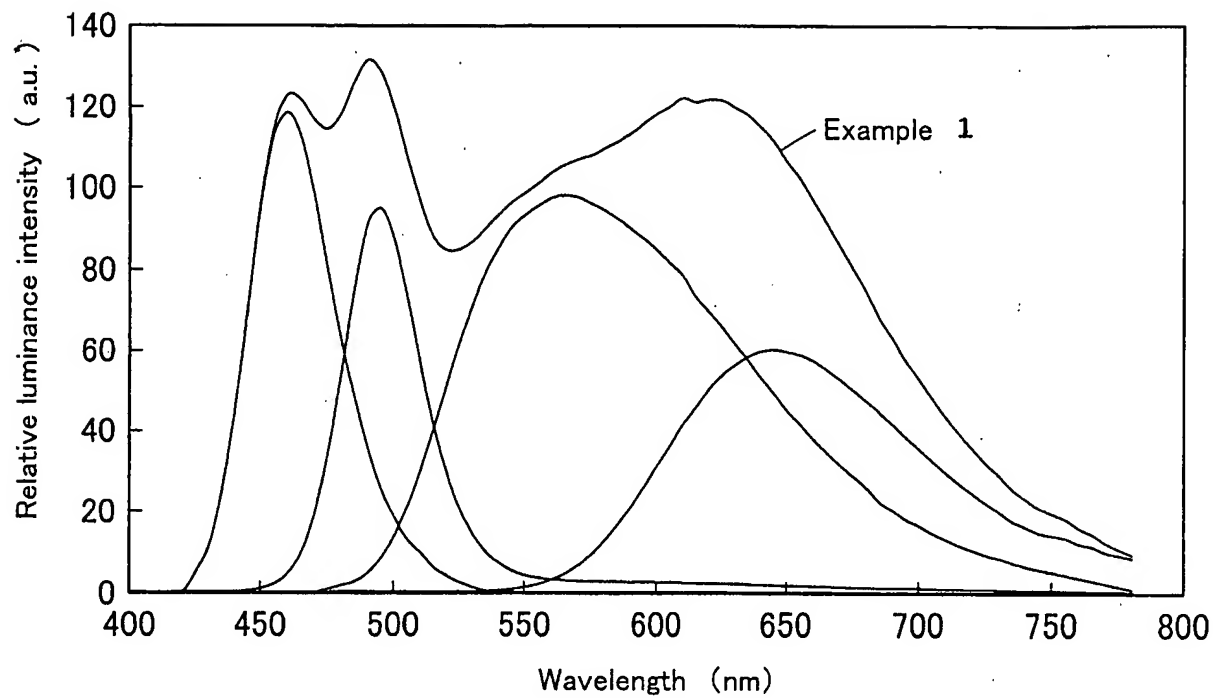
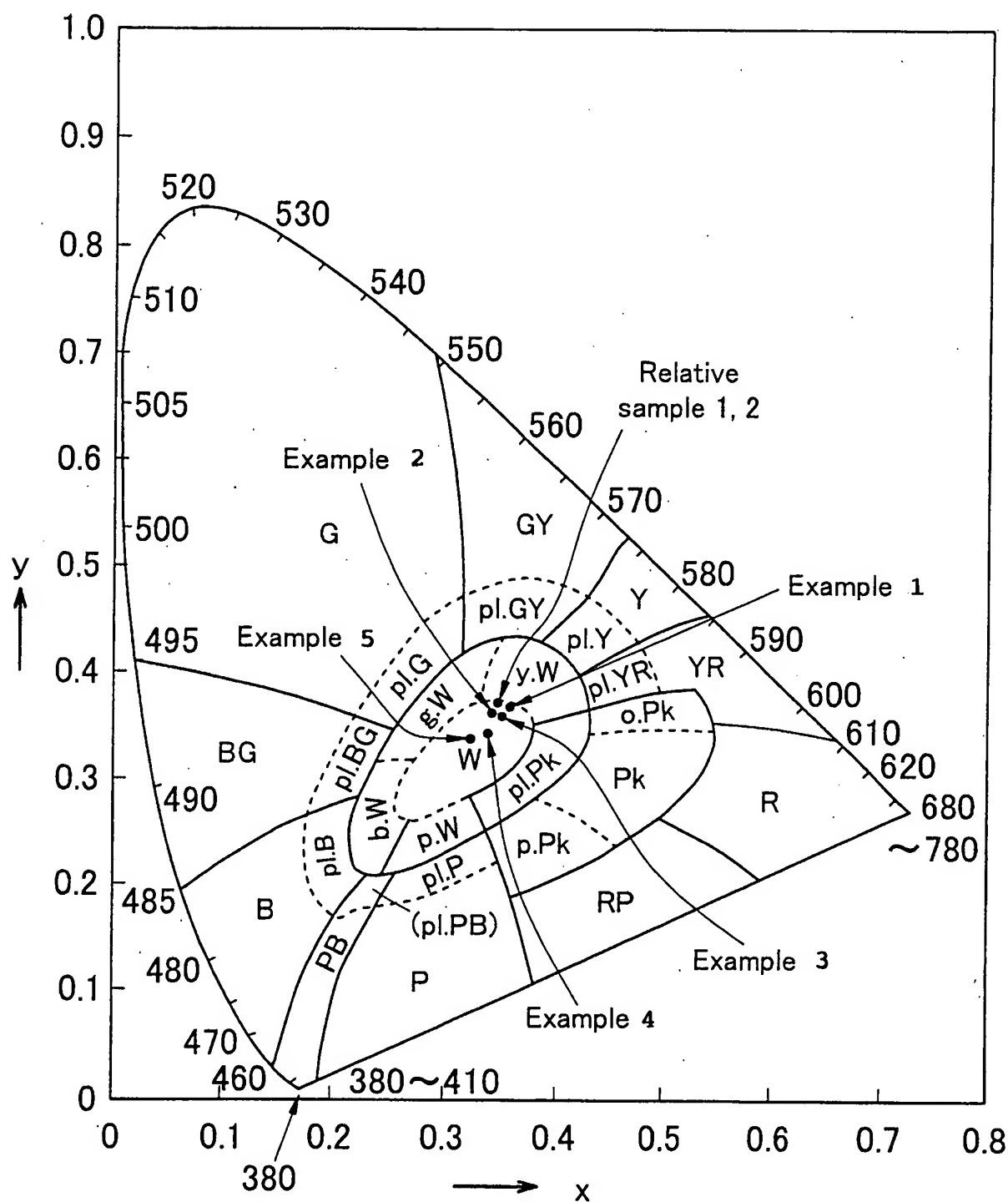


Fig. 12



G : Green	GY : Yellow green	pl.Y : pale yellow	b.W : Bluish white
Y : Yellow	YR : Yellow red	pl.G : pale green	g.W : Greenish white
R : Red	RP : Red purple	pl.B : pale blue	p.W : Purplish white
B : Blue	BG : Blue green	pl.P : pale purple	y.W : Yellowish white
W : White	PB : Blue purple	pl.Pk : pale pink	o.Pk : Orange pink
P : Purple	Pk : Pink	pl.PB : pale blue purple	p.Pk : Purplish pink
		pl.GY : pale yellow green	
		pl.BG : pale blue green	

Fig. 13

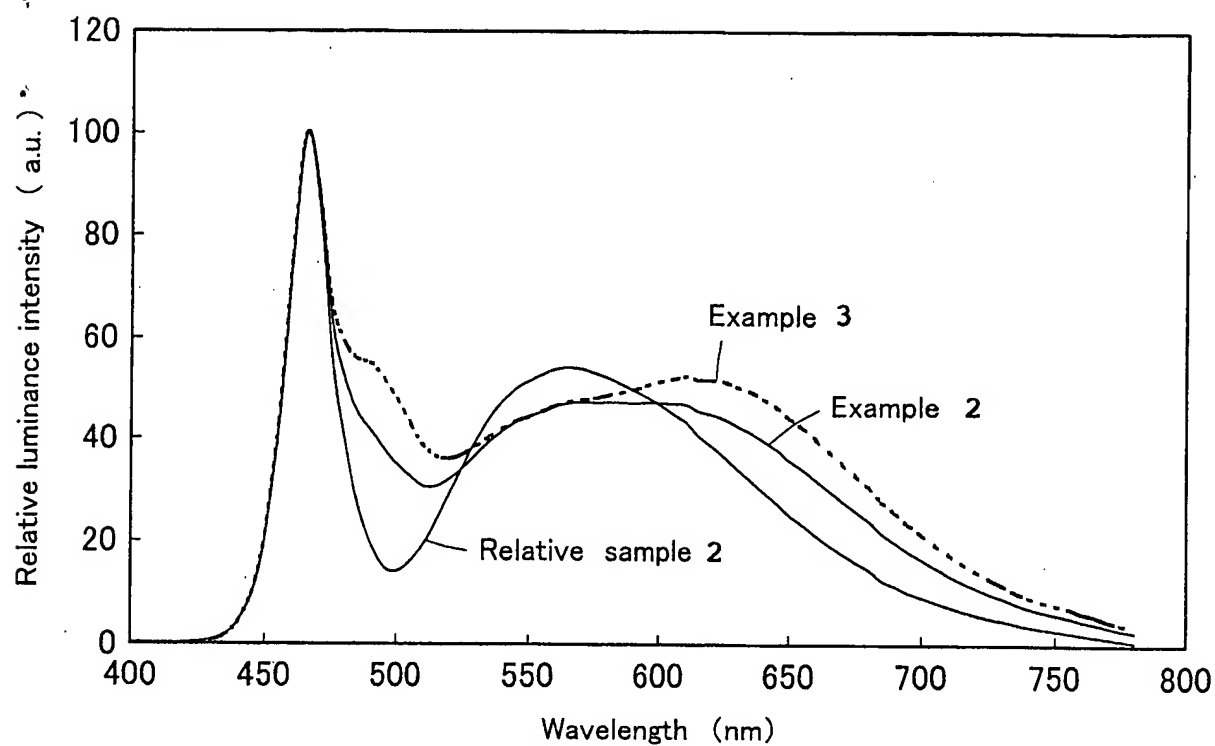


Fig. 14

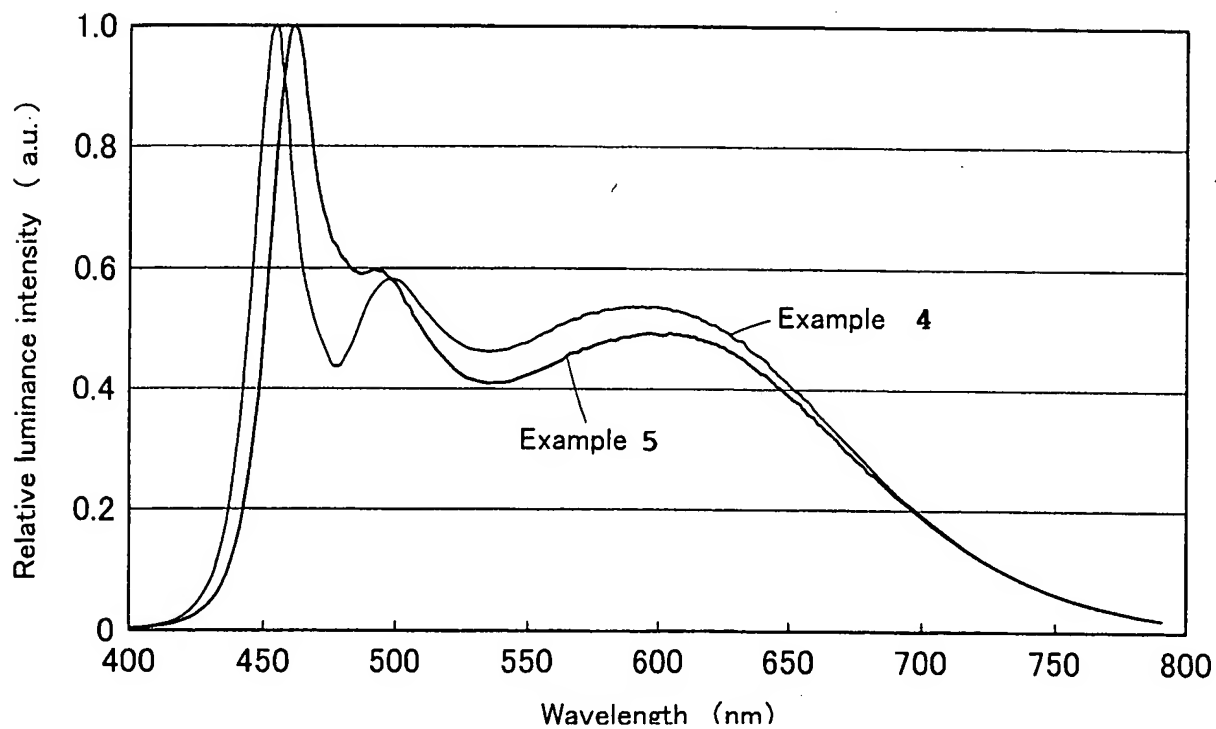
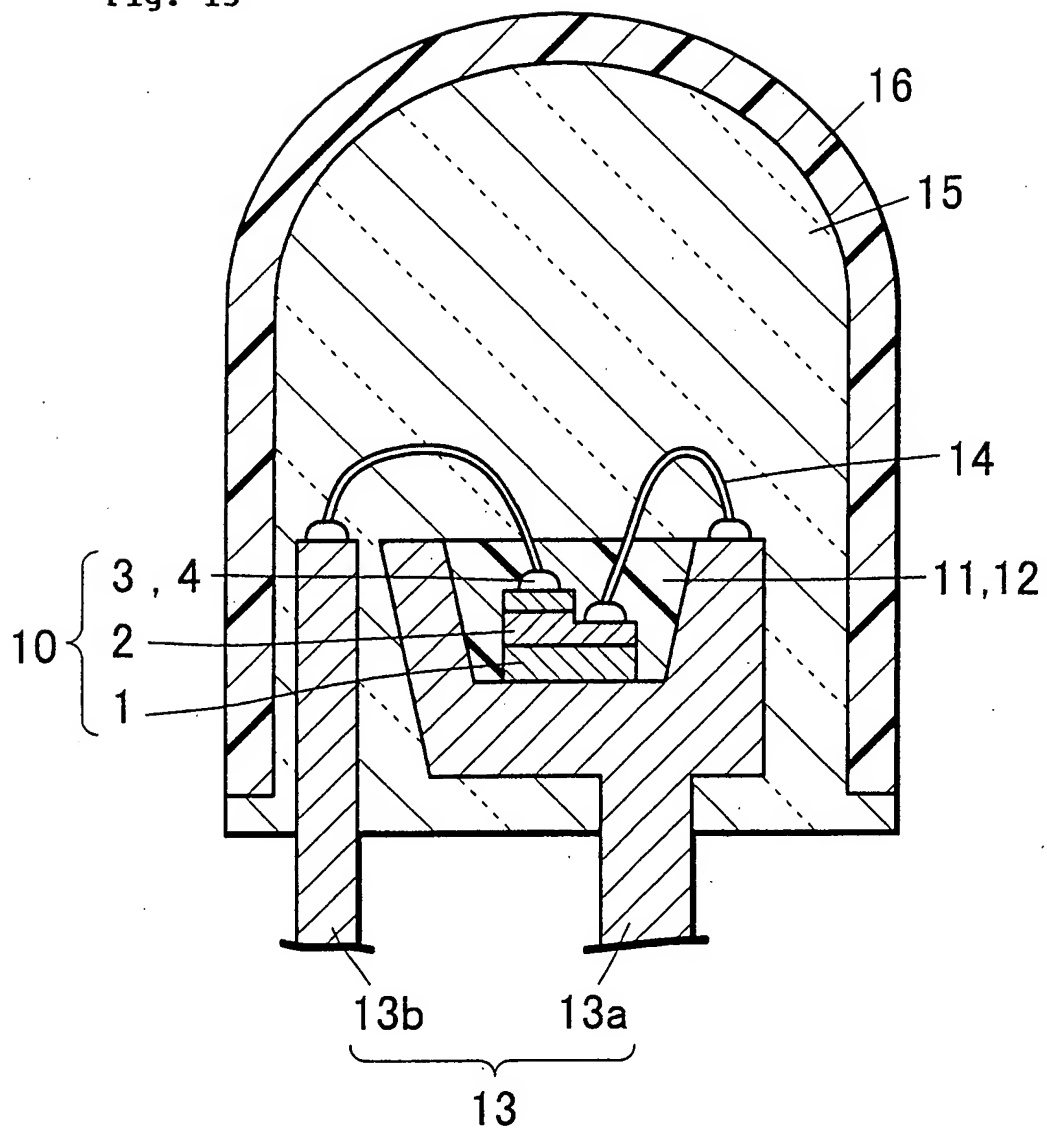


Fig. 15



[DOCUMENT] ABSTRACT

[Abstract]

[Problem to be solved] To provide a fluorophor subject to excitation by an excitation light source with ultraviolet to visible ray region and having luminescent color in a bluish green color to green color region subject to wavelength conversion.

[Solution] The oxynitride fluorophor is such that at least one rare earth element with Eu as the essential element is used as an activator R, essentially containing at least one group II element with Ba as the essential element selected from the group consisting of Ca, Sr, Ba and Zn, and at least one group IV element with at least Si as the essential element selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. In this fluorophor, the molar ratio: the group II element to R is (1:0.005) to (1:0.15).

[Selected Figure] Fig. 14

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